Surface-related optical properties of GaN and InGaN nanocolumns.

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[2]: *OSRAM Opto Semiconductors GmbH. Regensburg, Germany.*

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** :* Present address: *Laboratoire Charles Coulomb-CNRS-University of Montpellier II, France.*

OUTLINE

The 3.450 – 3.457 eV doublet. The 3.474 eV line…

The *Peculiar Physics of Donor-Bound Excitons in GaN NCs*

Surface Related PL Quenching Effects

- GaN NCs (and model)

- InGaN NCs

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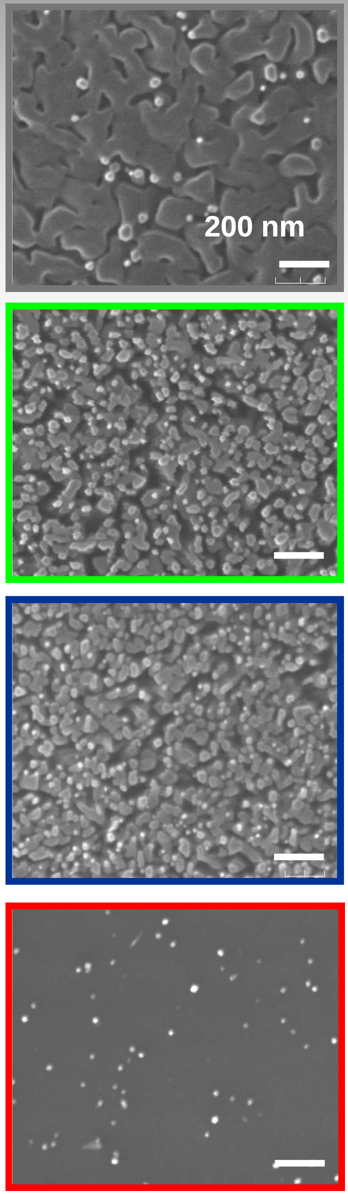
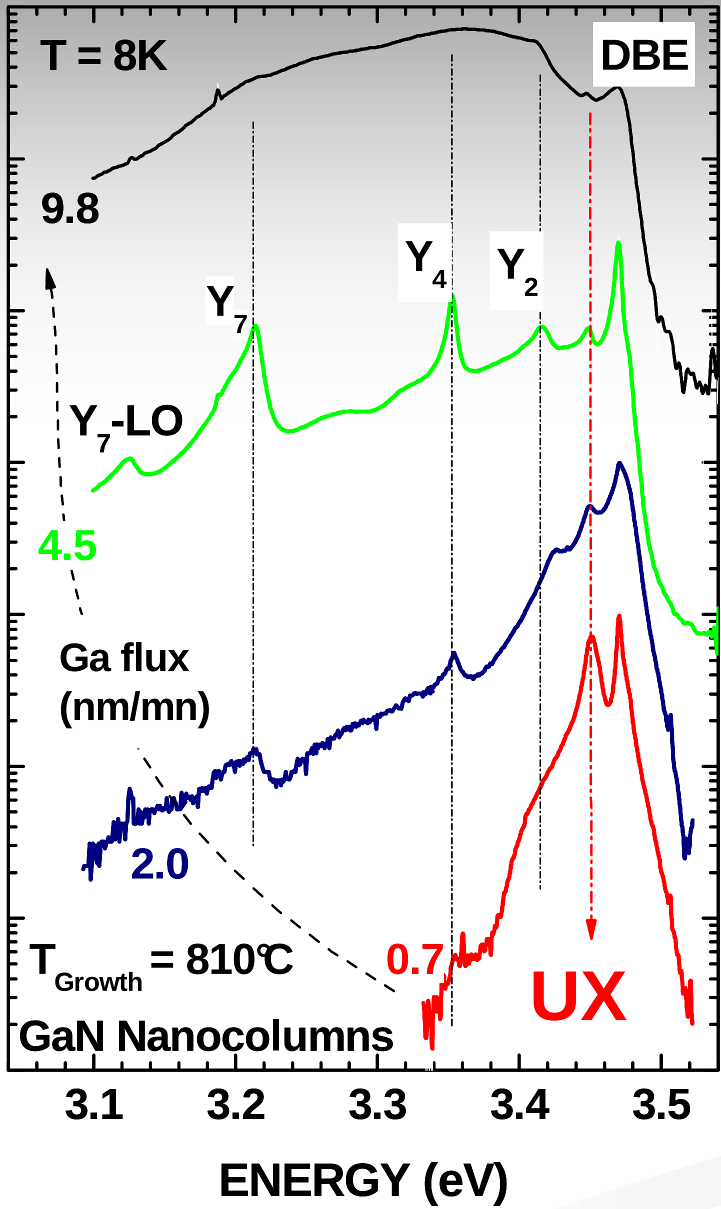
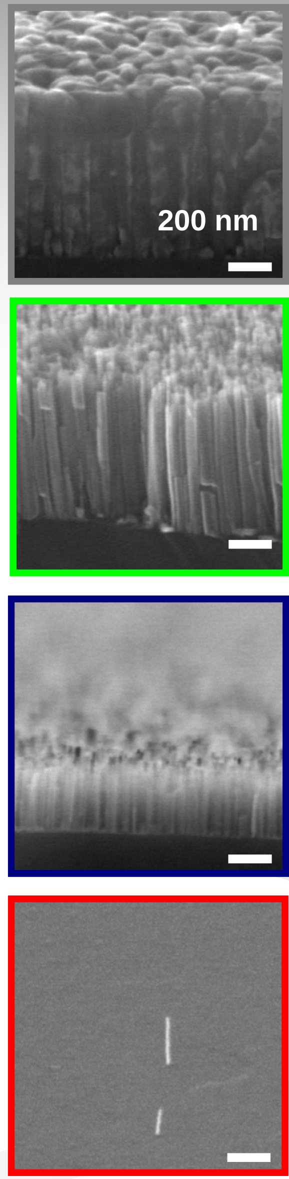
Surface – Related Excitonic Lines

A Strange Defect



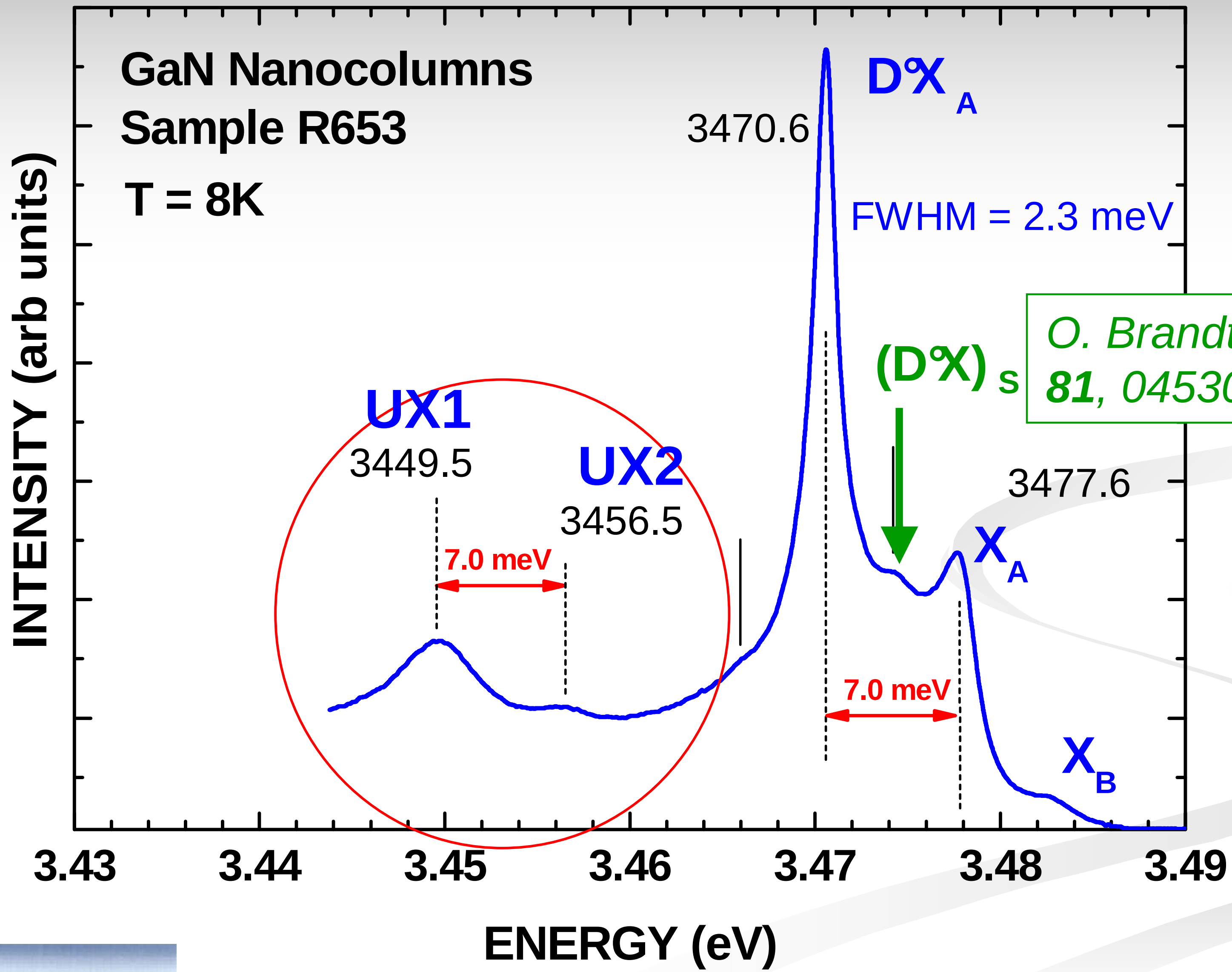




- GaN NCs on Si
- PA-MBE
- Diameters 20 – 60 nm
- Lengths 0.6 – 1.2 µm
- Unstrained
- PL lines correlate to NC coalescence, ***EXCEPT* the 3.45 eV doublet**

Lefebvre et al. Appl. Phys. Lett. ***98****, 083104 (2011)*

PL of Dense Ensemble of GaN NCs



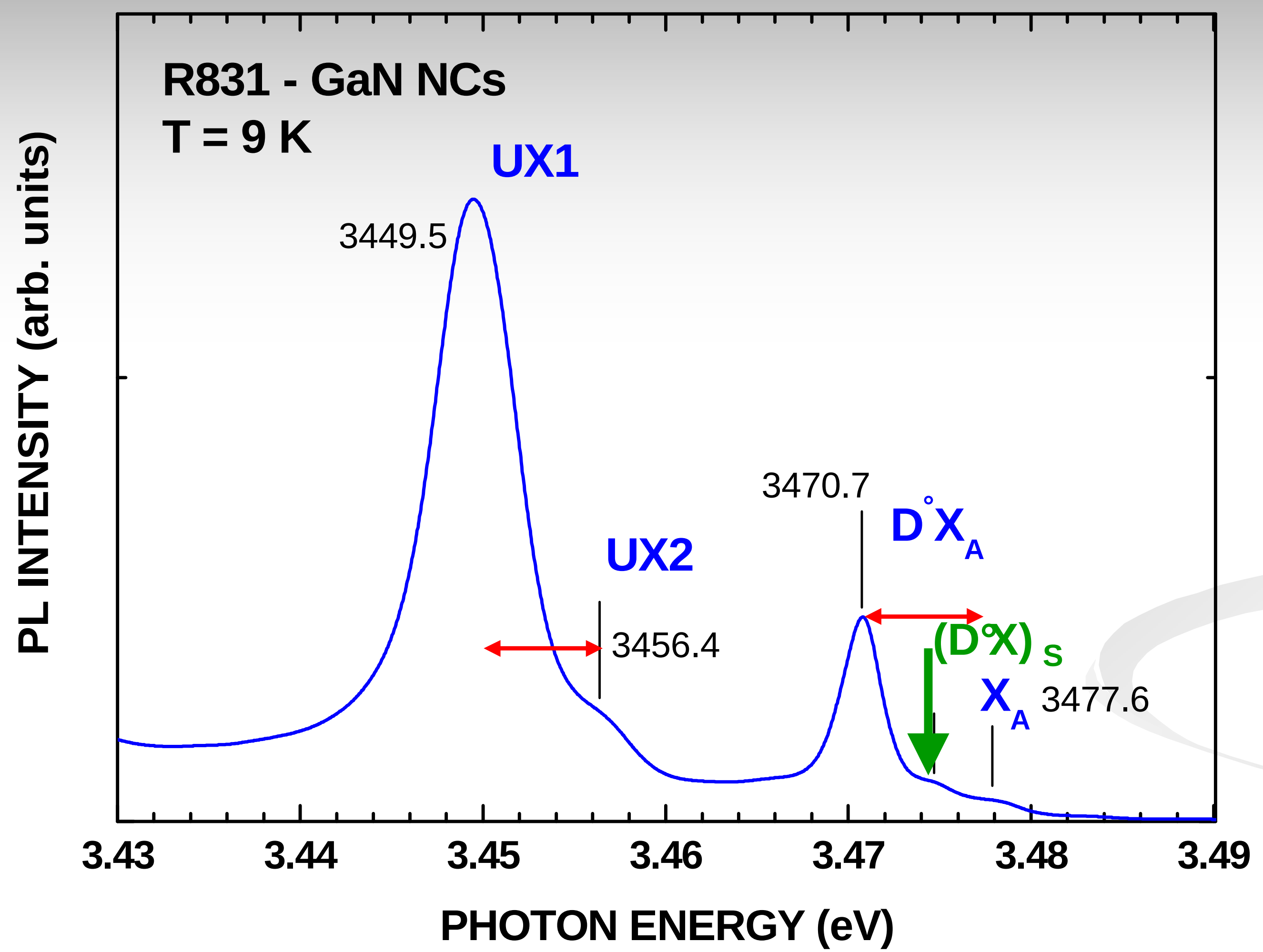
O. Brandt et al. PRB ***81****, 045302 (2010)*

Two lines separated by

7 meV.

Sometimes dominated by D°X / X $_{A}$.

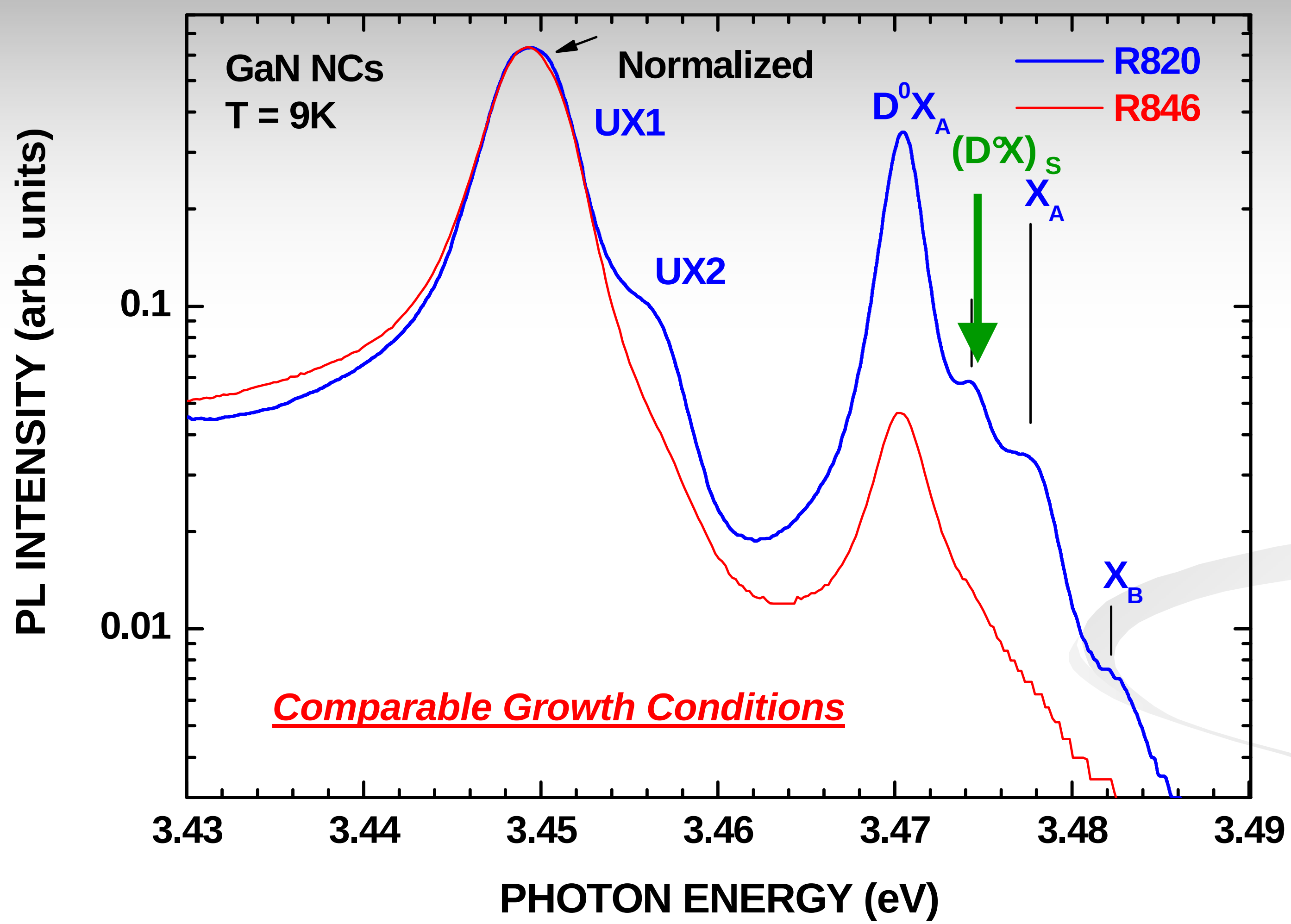
PL of Dense Ensemble of GaN NCs



…Sometimes dominant.

All peaks always at the same energy: no strain.

PL of Dense Ensemble of GaN NCs

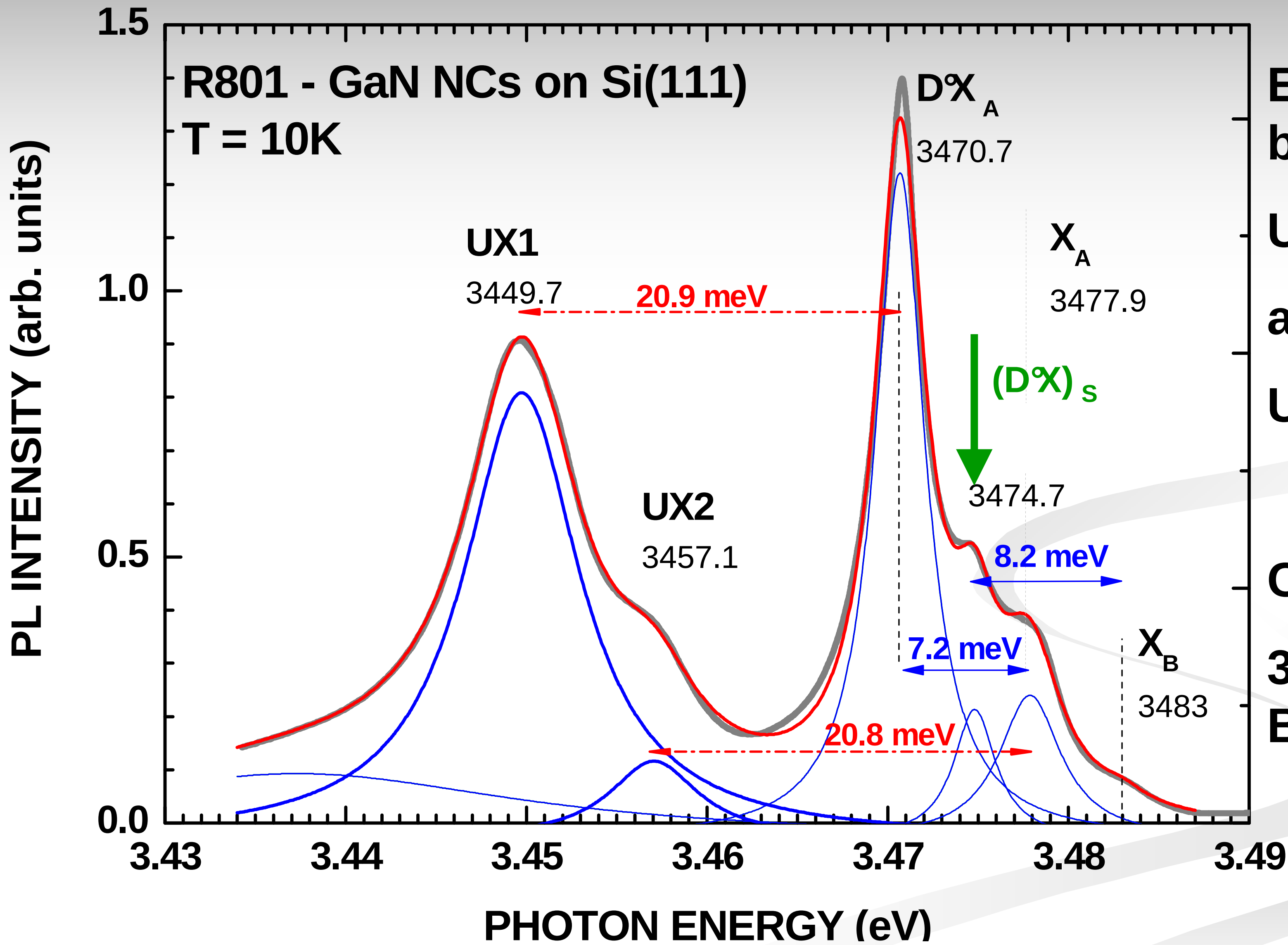


Not easily correlated to diameters or densities… or growth parameters.

When FX lines vanish,

UX2 vanishes too.

Deconvolution of Excitonic PL



Energy difference between

UX1 - D^0X_A

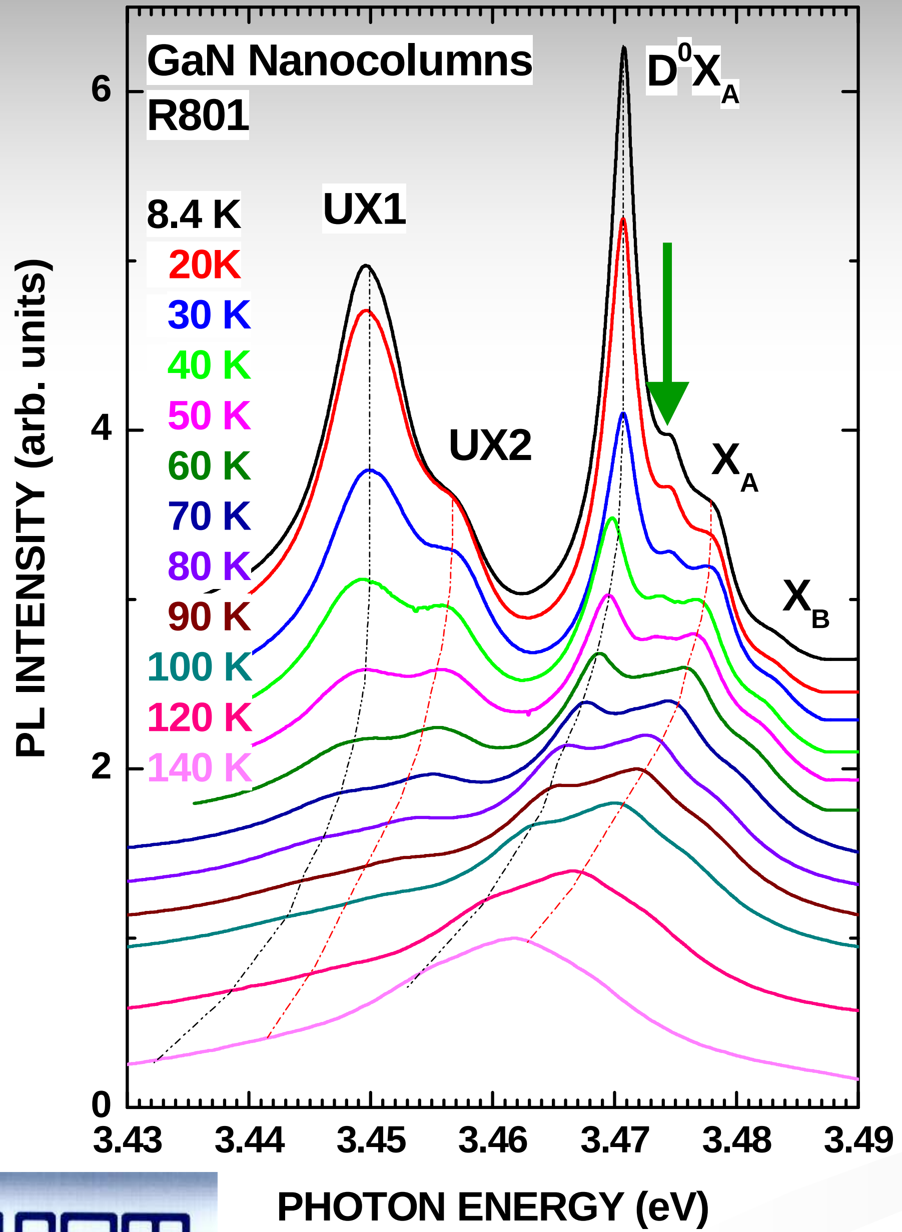
and

UX2 – X_A

Comparable to

3/4 of Donor Binding Energy

Excitonic PL *vs* Temperature



D^0X looses rapidly intensity to the benefit of X_A and X_B.

Likewise,

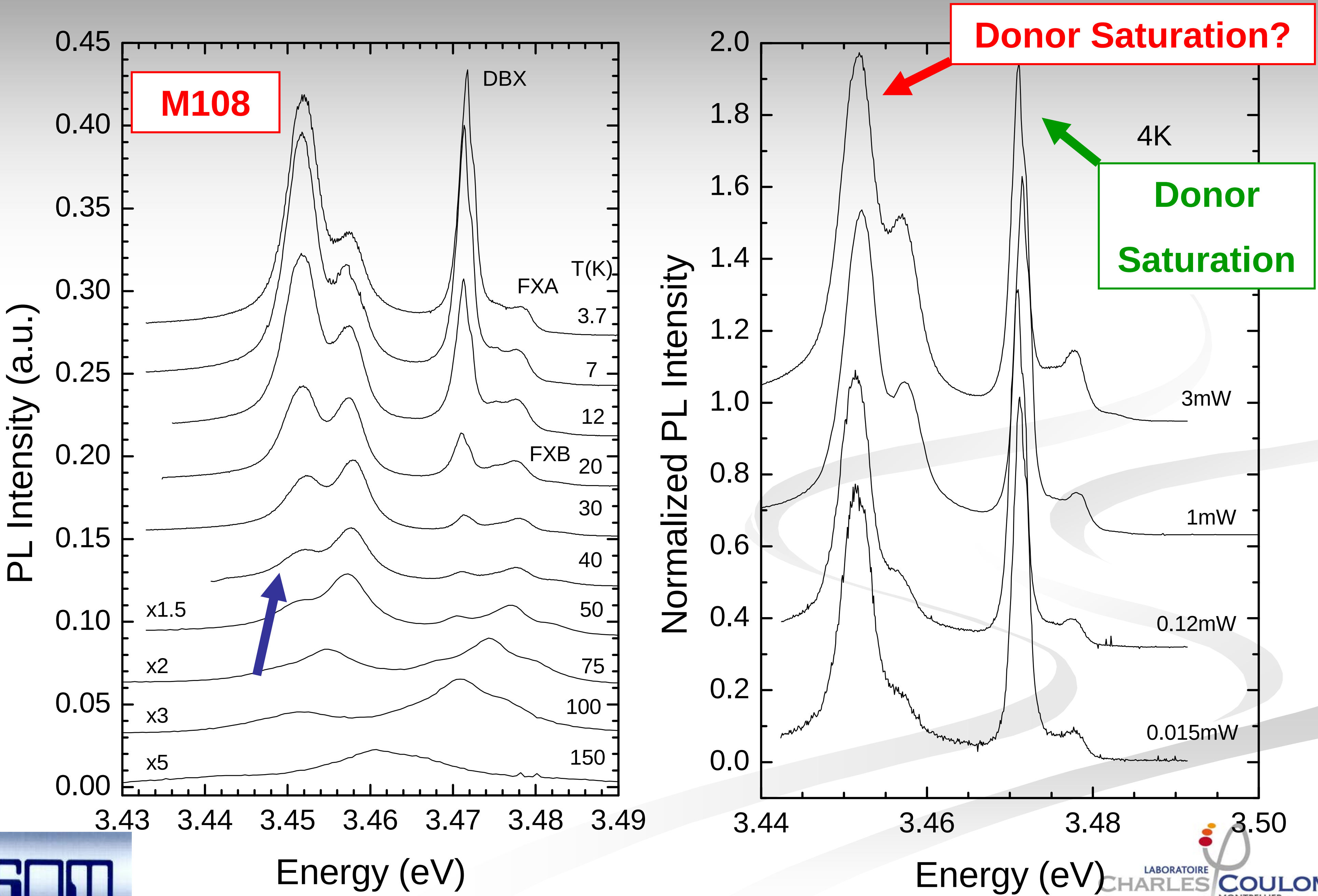
UX1 looses rapidly intensity to the benefit of UX2.

Suggestion:

UX1 linked to D^0X

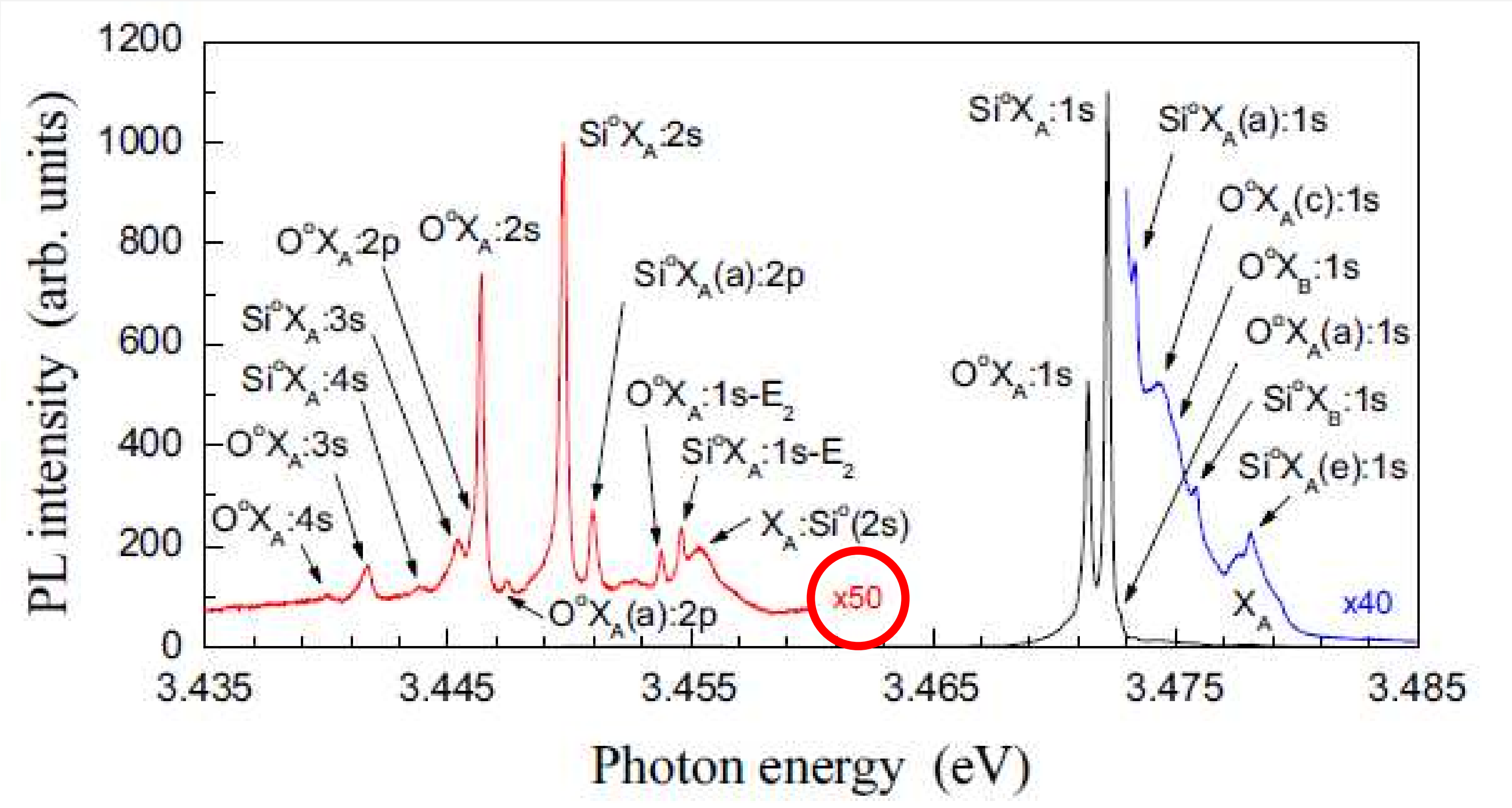
UX2 linked to free exciton X_A

Effect of T – Effect of Power



Proposal: Surface-Enhanced TES

Energies are consistent with TES in bulk GaN.
First, discarded because too intense *[Calleja et al. PRB **62**, 16826 (2000)].*
Re-examined with Core-Shell Model *[Corfdir et al. JAP 105, 013113 (2009)].*



*Paskov et al. Phys. Stat. Sol. (c) **4**, 2601 (2007)*

HVPE 1 mm-thick GaN epilayer. $n \sim 10^{16}$ cm^{-3}. (D^0X at 3.472 eV).

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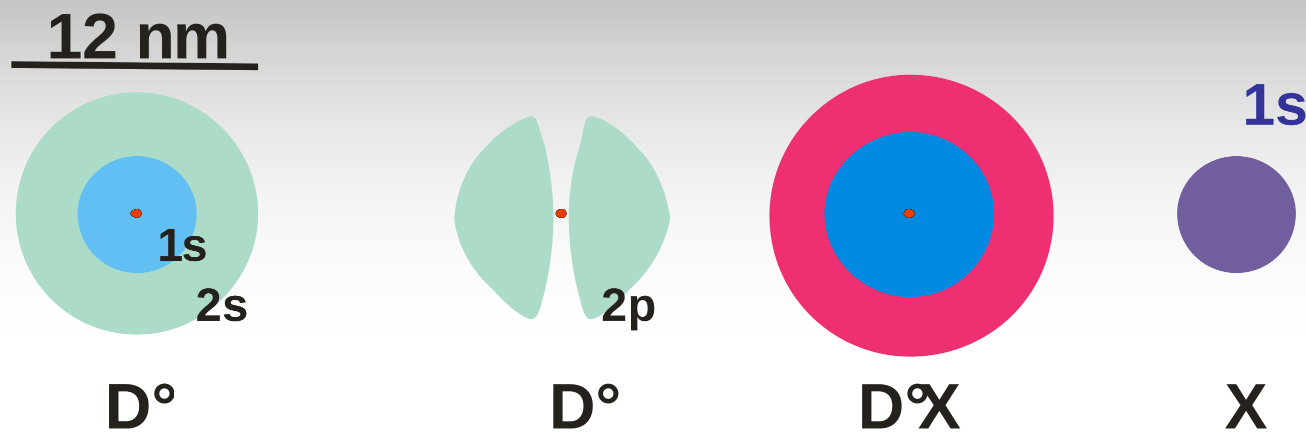
Zoology of Donor and Exciton States

1s: ~30 meV



1s: ~26 meV

2s, 2p: ~7.5 meV

30 + 26 + 7 = 63 meV

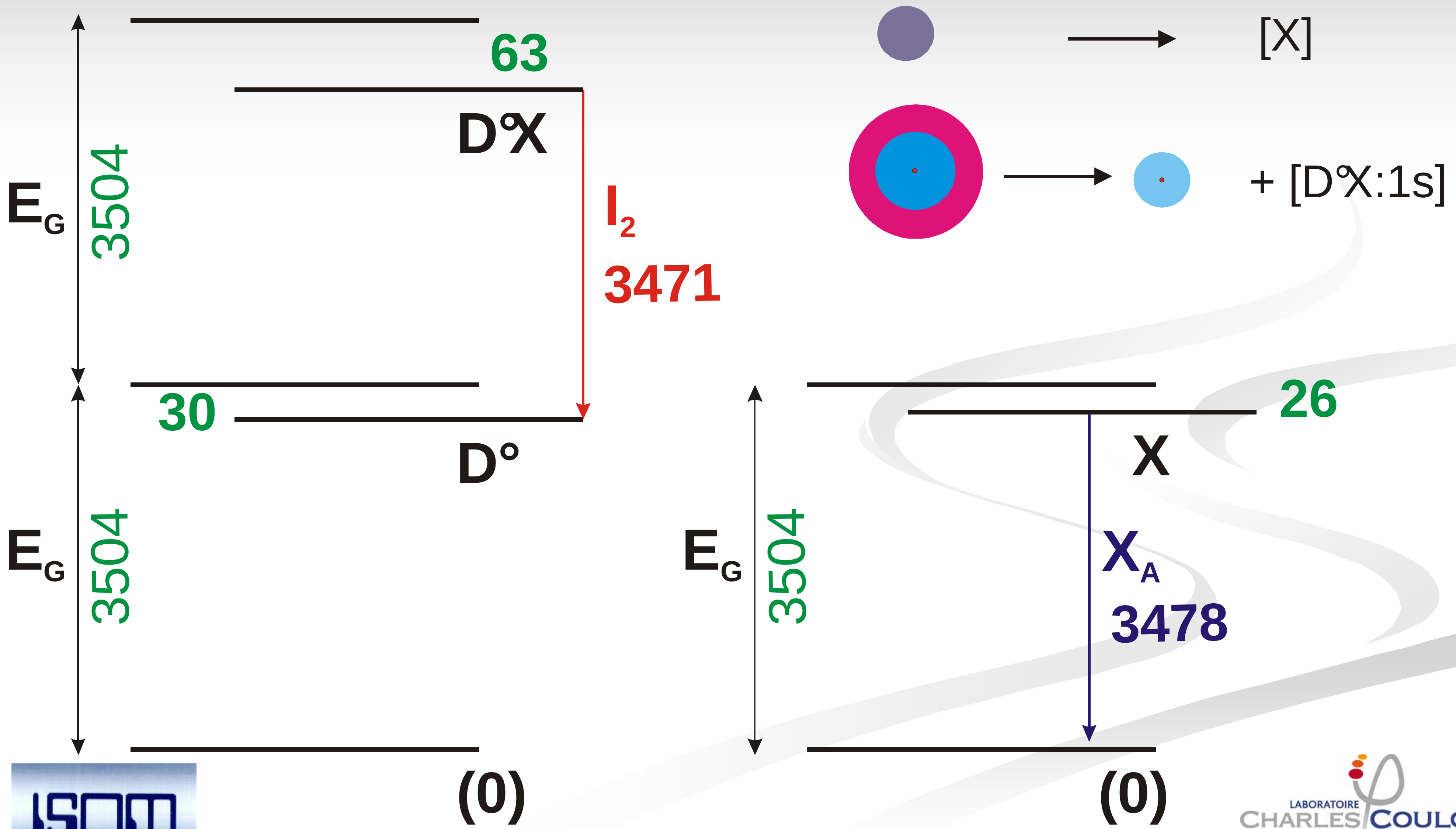
Remark : D°X has excited states, named rotational states (a, b, c…)
Separation of typically 1-2 meV…
Essentially excited orbitals of hole.

G. Neu et al., Phys. Stat. Sol. 216, 79 (1999) ; Phys. B 302, 39 (2001).

*B. Gil et al., PRB **75**, 085204 (2007)*

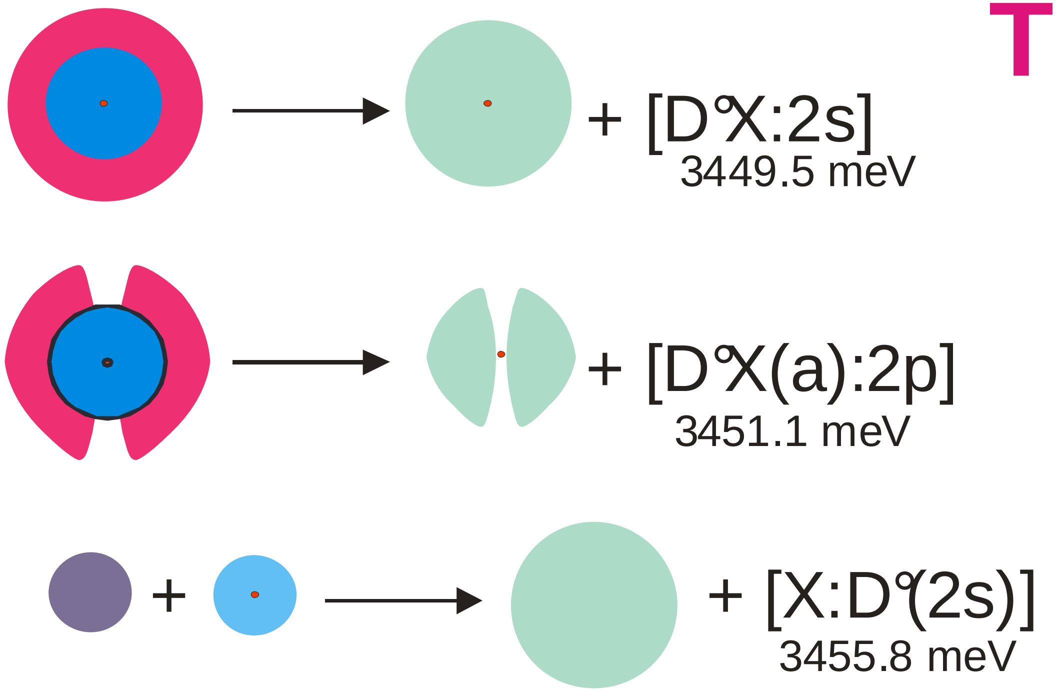
Zoology of Donor and Exciton States

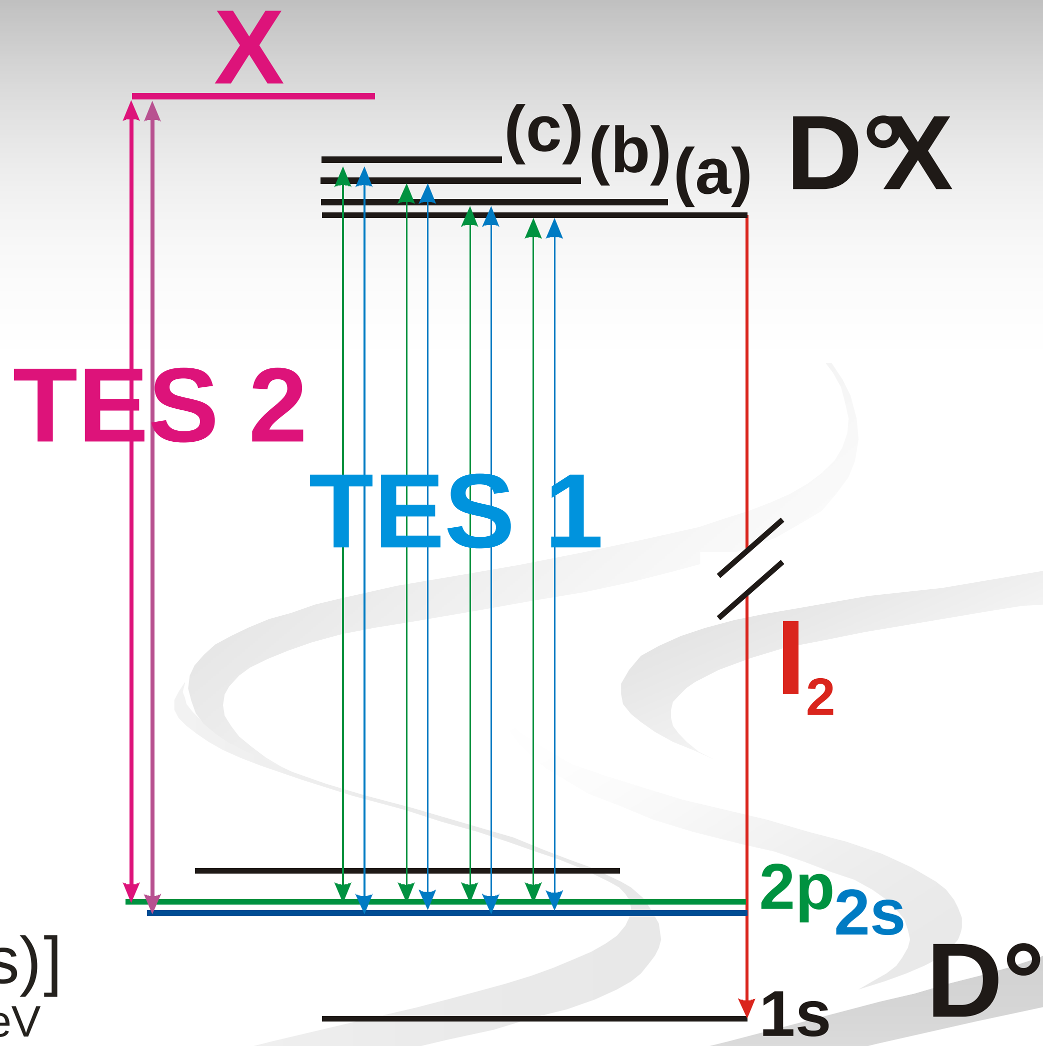
Dominant lines: X_A and I_2



Zoology of Donor and Exciton States

Satellite lines: TES





Origin of Relative Intensities: Symmetries

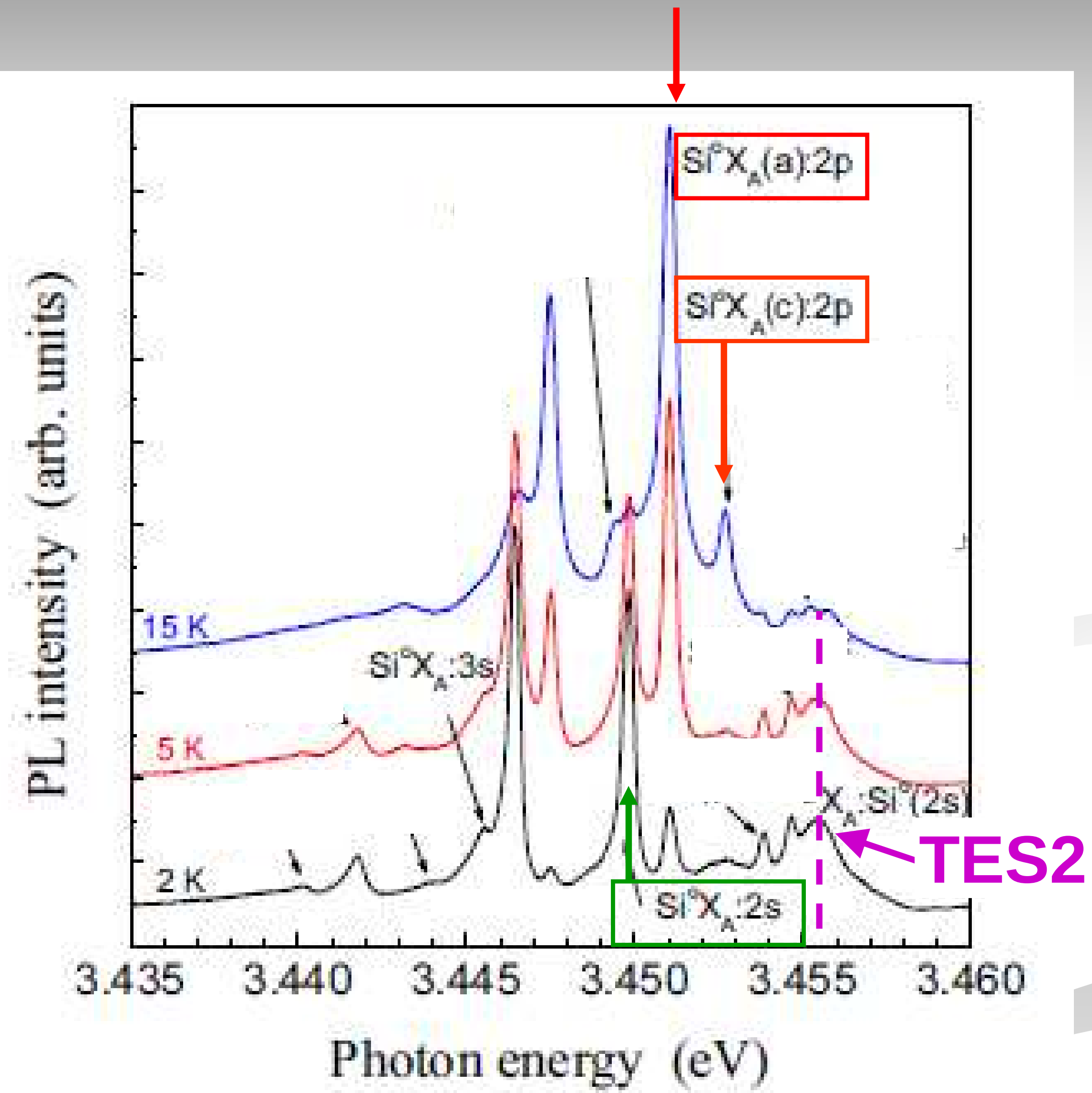
When T is increased so that (a) and (c) excited states of D^0X are populated,

D^0X:2s transition transfers oscillator strength to

D^0X(a):2p and **D^0X(c):2p** .

Reason:

Compatible Symmetries.



*Paskov et al. Phys. Stat. Sol. (c) **4**, 2601 (2007)*

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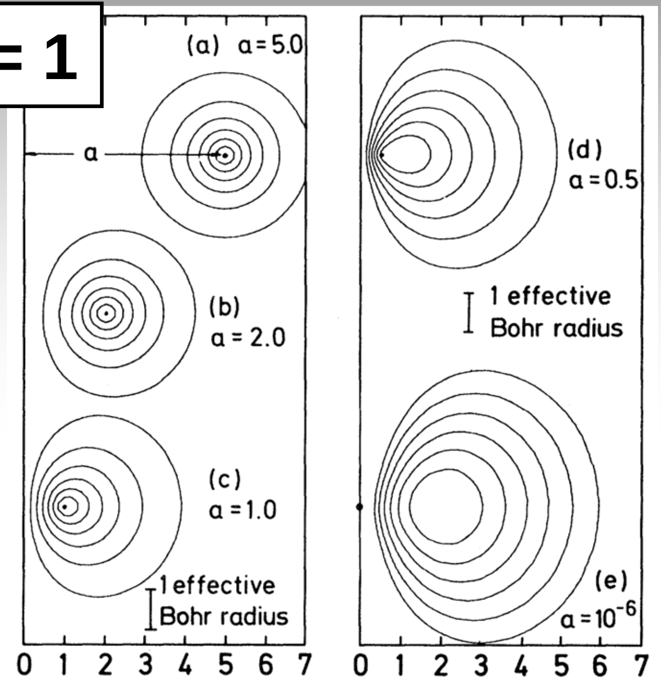
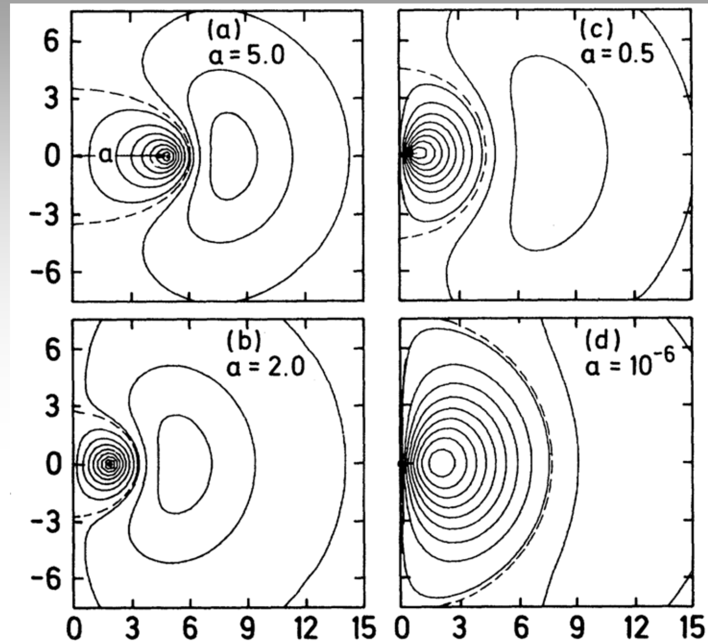
Donor States Near a Surface: Wave Functions

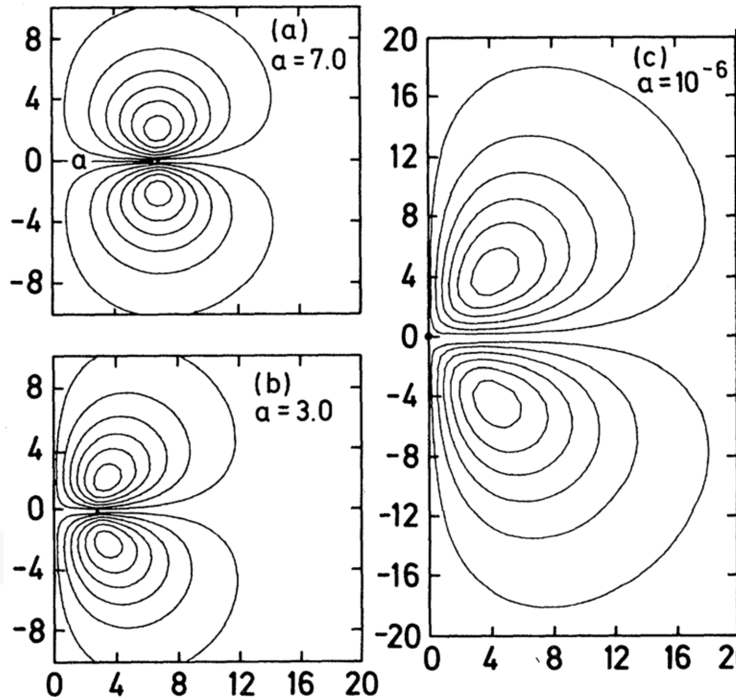
n = 1



n = 2
m = 0



n = 2
m = 1



Wave functions are perturbed for donor lying in Surface Region of:

- **(n = 1) : ~6-9 nm in GaN**
- **(n = 2) : ~ 15-18 nm in GaN**

*S. Satpathy PRB **28**, 4585 (1983)*

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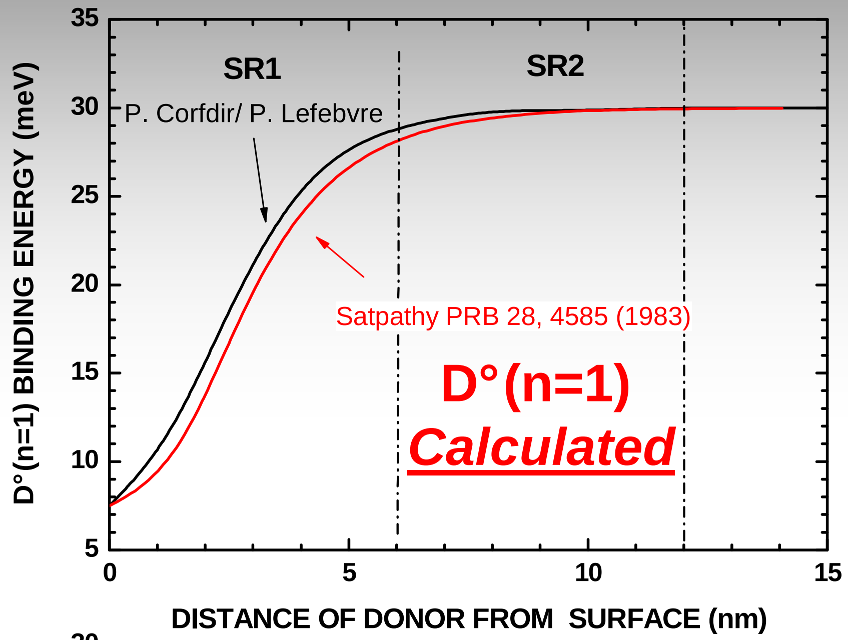
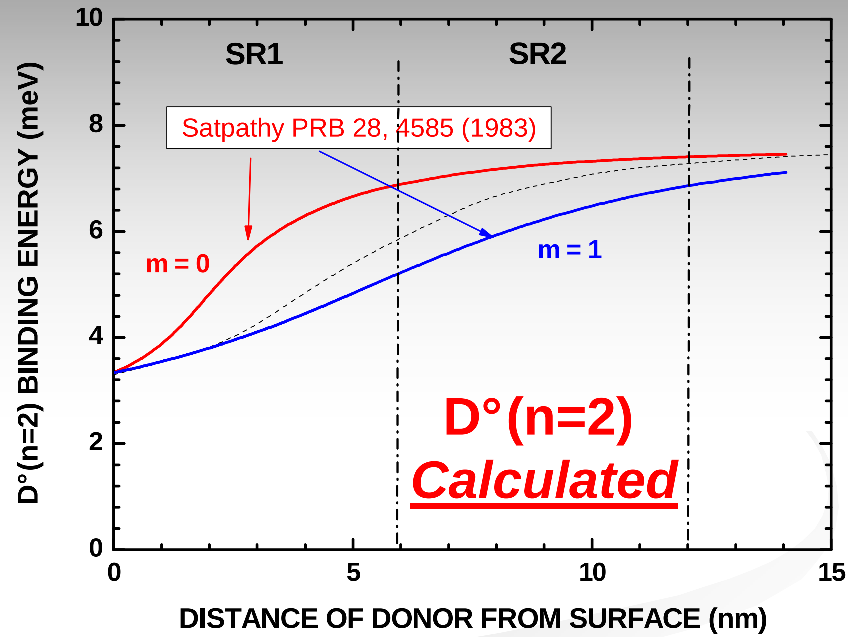
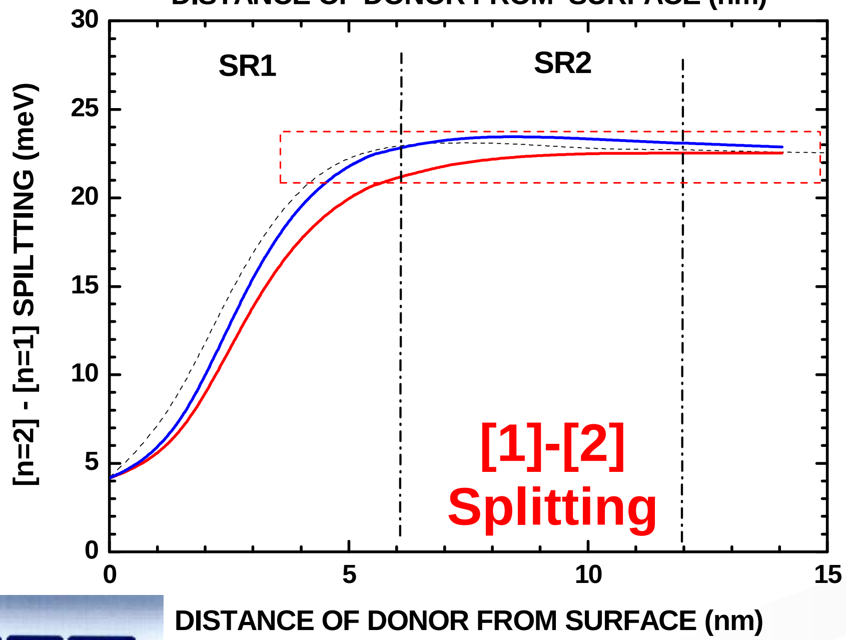
Donor States Near a Surface: Energies







SR1: Both energies and wave-functions of D°are changed.

SR2: Energies are comparable to those in bulk, but wave-functions are still distorted.

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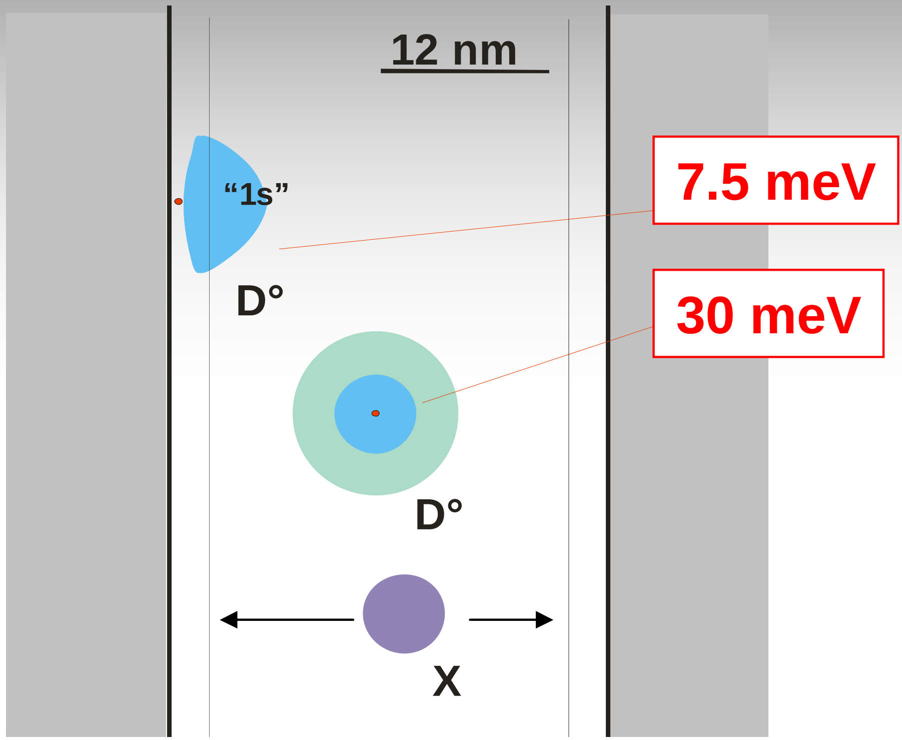
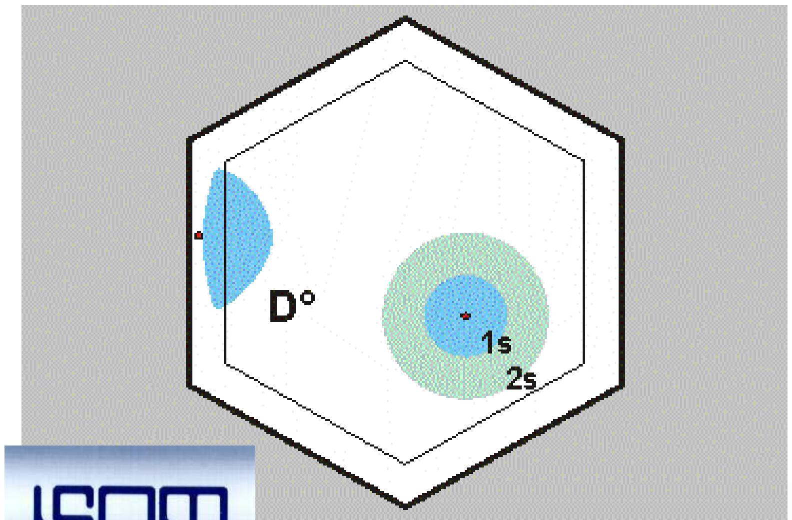
GaN Nanocolumns: Surface Region #1 (SR1)





NOT accessible to FX Center of Mass

Typical SR1 width of ~5-6 nm.

When the Donor lies in **SR1**,

- 7.5 < E_B < 30 meV
- Reduced Symmetry of ground state
- ***So is*** the symmetry of D°X states.

Line at 3474 meV (↓) : D°X $_S$

*O. Brandt et al. PRB **81**, 045302 (2010)*

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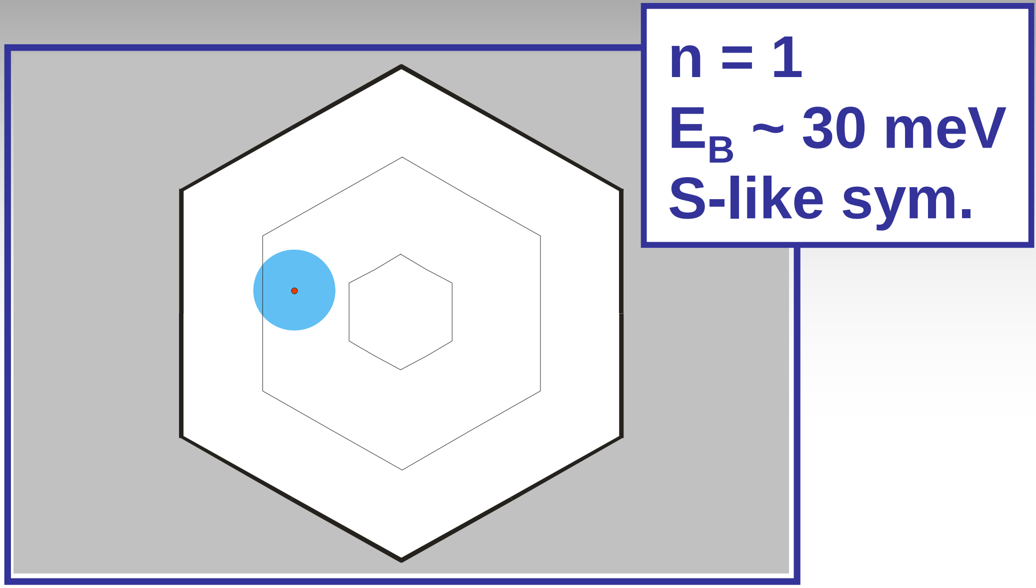
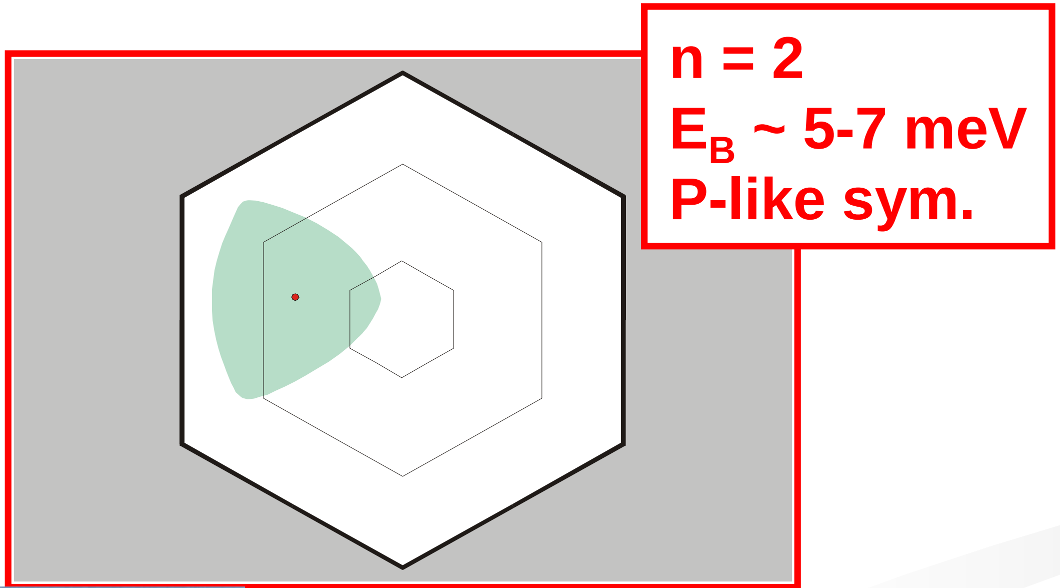
GaN Nanocolumns: Surface Region #2 (SR2)





When the Donor lies in SR2,

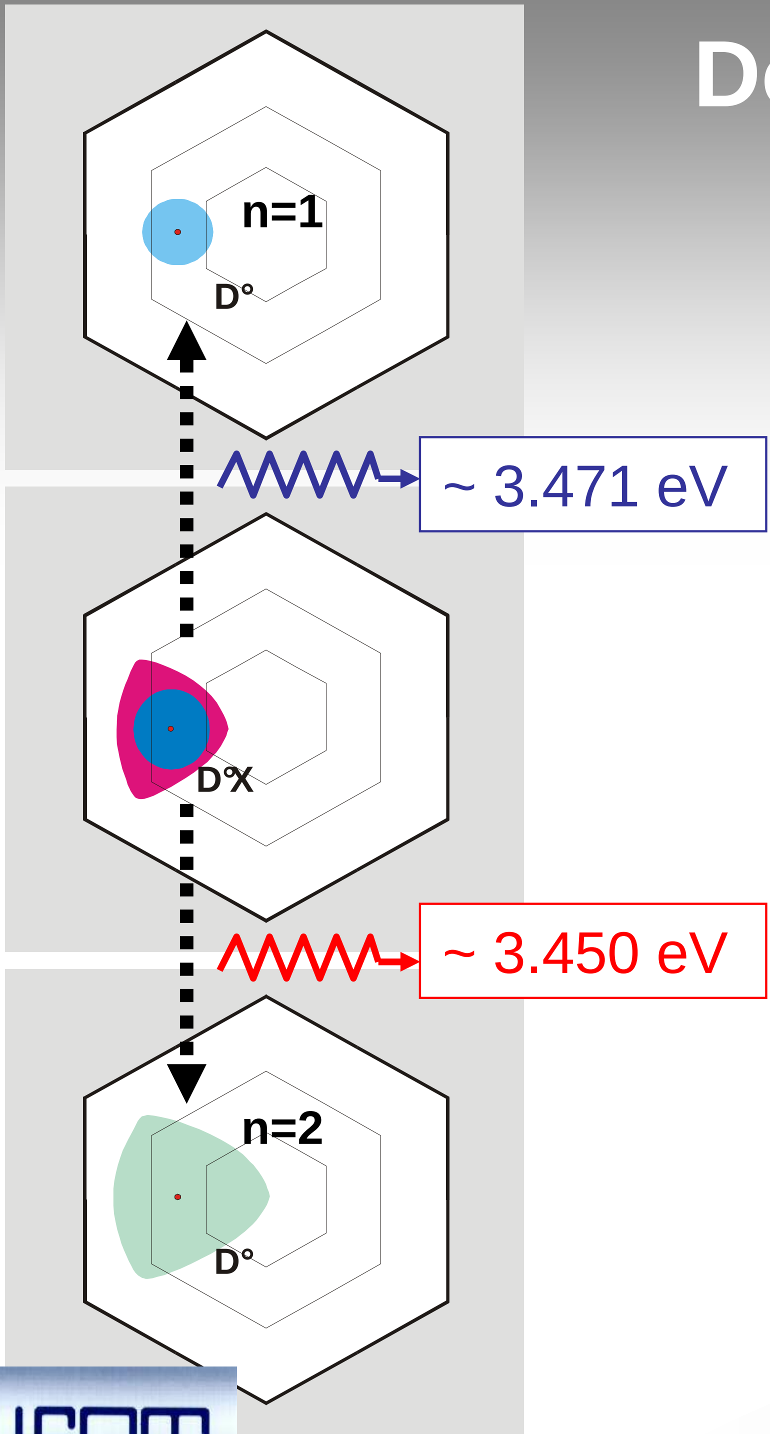
D° Ground State nearly unchanged

Altered Wave-Functions:

- Excited states (2s, 2p…)

- D°X states

Donor in SR2 (~6 to 15 nm)



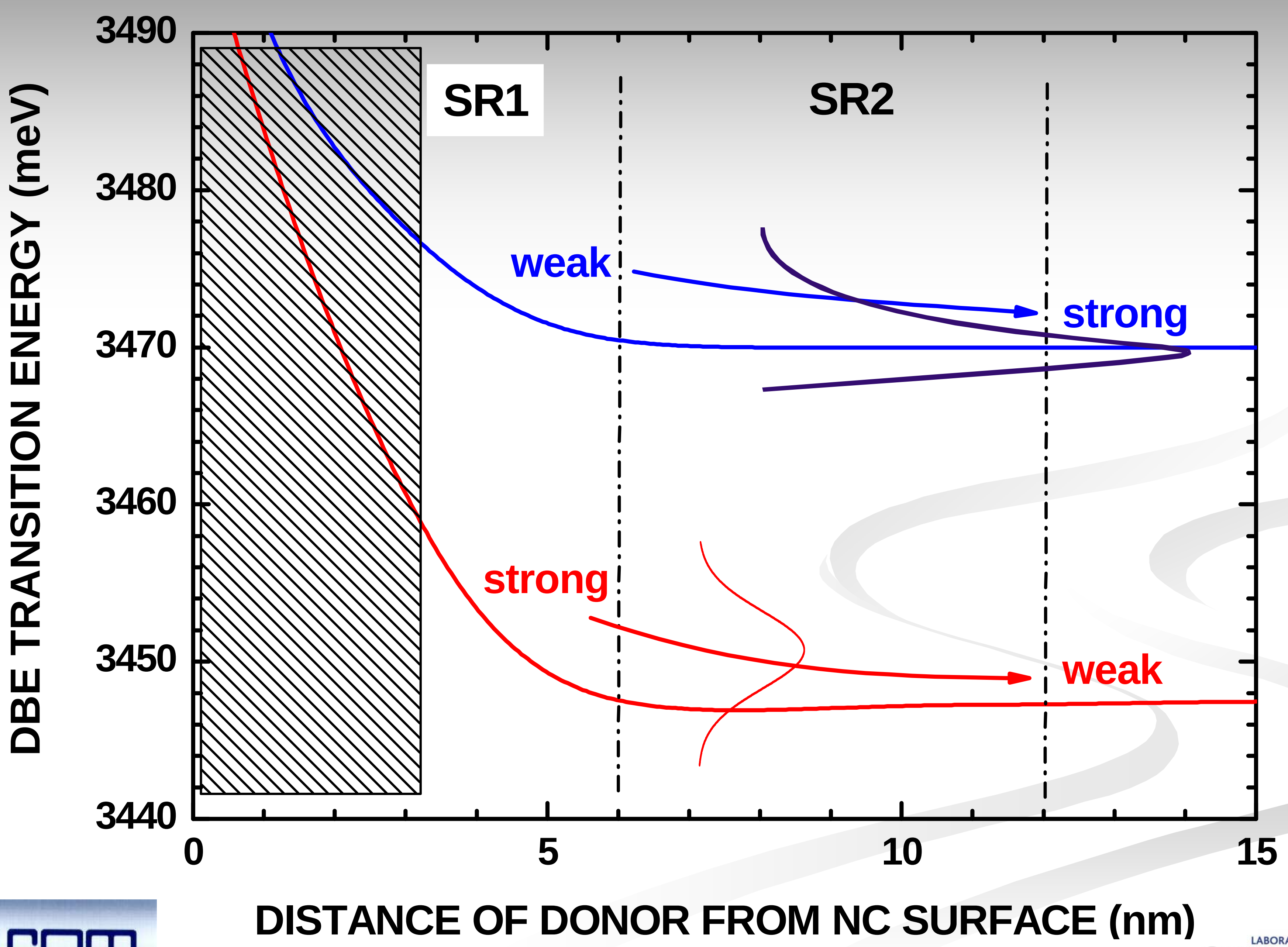
D°X stable with cohesion energy slightly lower than 63 meV, ***<u>AND</u>***
Wave functions deformed by surface.

D° Excited states (n=2) of D° perturbed by surface, ***<u>AND</u>***
[1-2] splitting of 21-24 meV.

D°X hole wave function overlaps better with [n=2] than with [n=1]

<u>SATELLITE LINES MORE INTENSE</u>

Donor-Bound Exciton Transitions in GaN NCs



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Surface – Related,

Room-Temperature

PL Quenching

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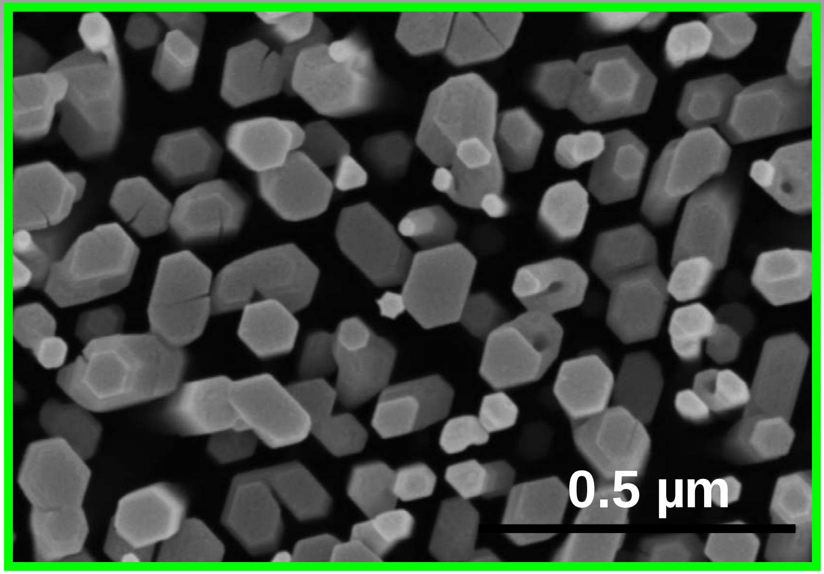
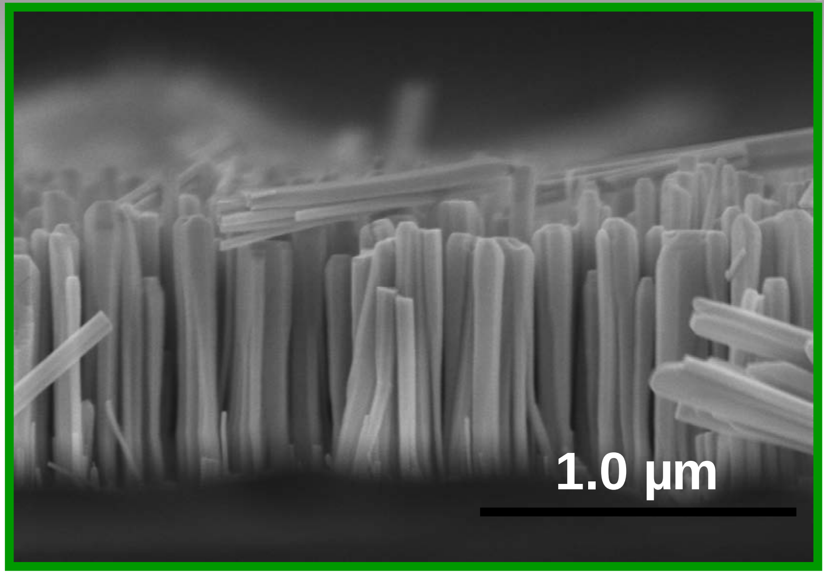
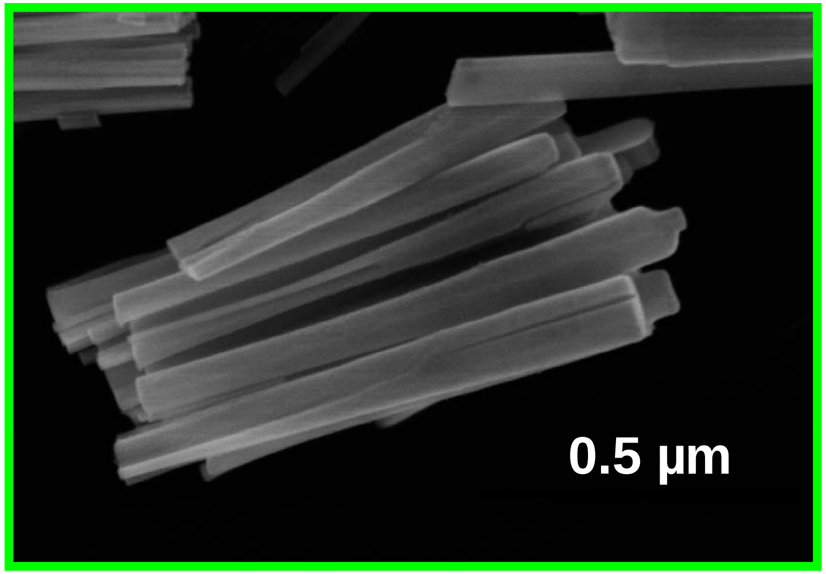
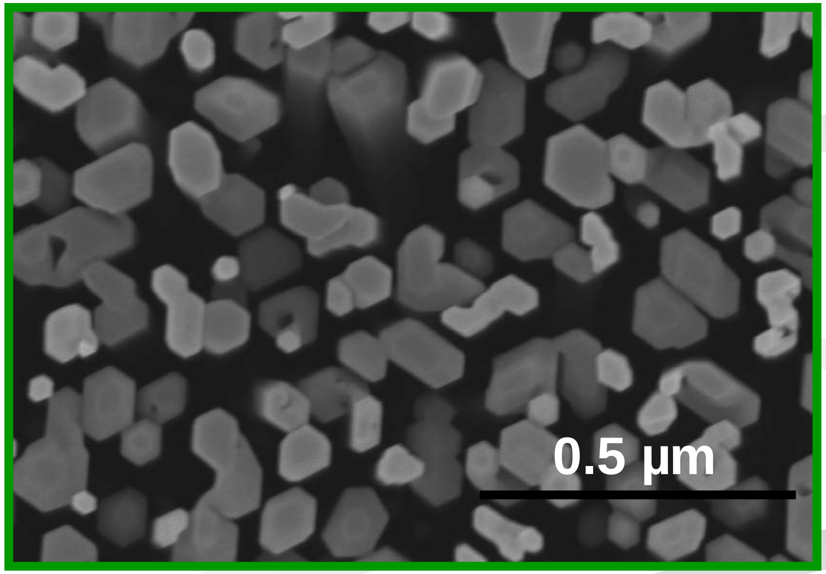
GaN – InGaN Nanocolumns: Morphology







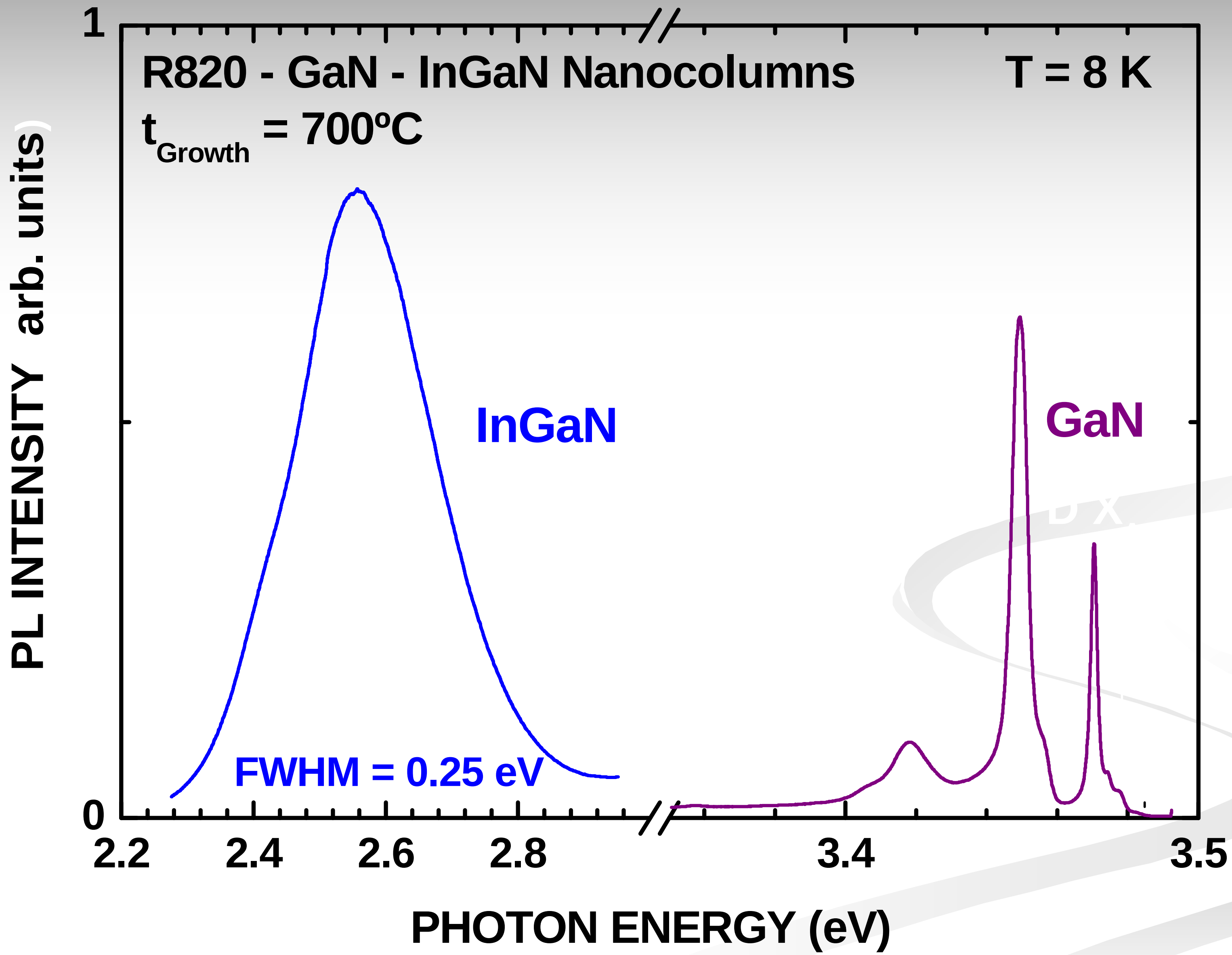


T_{Growth} = 675℃
x_{In} = 0.28

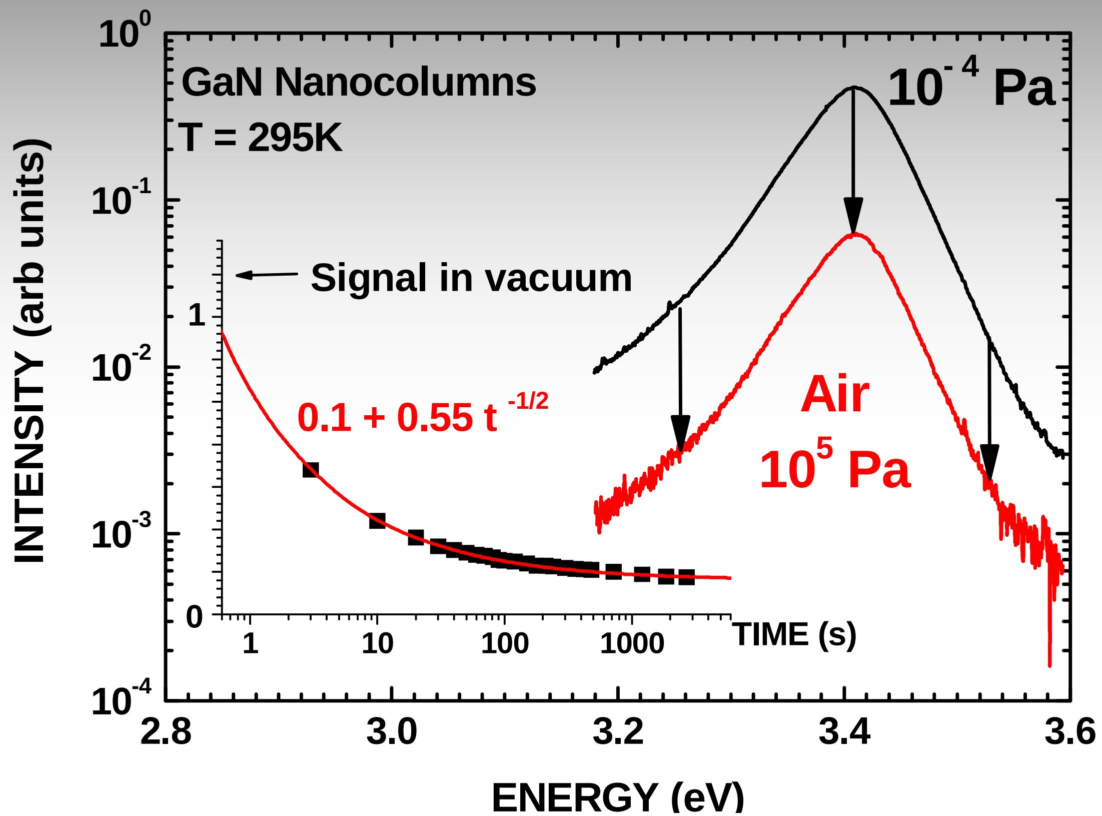
U. Jahn
PDI, Berlin

T_{Growth} = 700℃
x_{In} = 0.19

Low-Temperature PL Spectrum: GaN and InGaN



GaN Nanocolumns: Excitonic PL Quenching in Air



- Identical in ALL GaN NC samples
- NO Change in Spectrum
- Does NOT occur with pure N_2
- Reversible
- Effects induced by *laser excitation*

⇒ **Self-limited Photoabsorption / Photodesorption of Oxygen**

Similar Effects Reported for

GaN Layers: *M.A. Reshchikov et al., J. Vac. Sci. Technol. B* ***27****, 1688 (2009)*

ZnO Nanowires: *M. Foussekis et al., APL* ***94****, 162116 (2009)*

GaN Nanowires: *C. Pfüller et al., Phys. Rev B* ***82****, 045320 (2010)*

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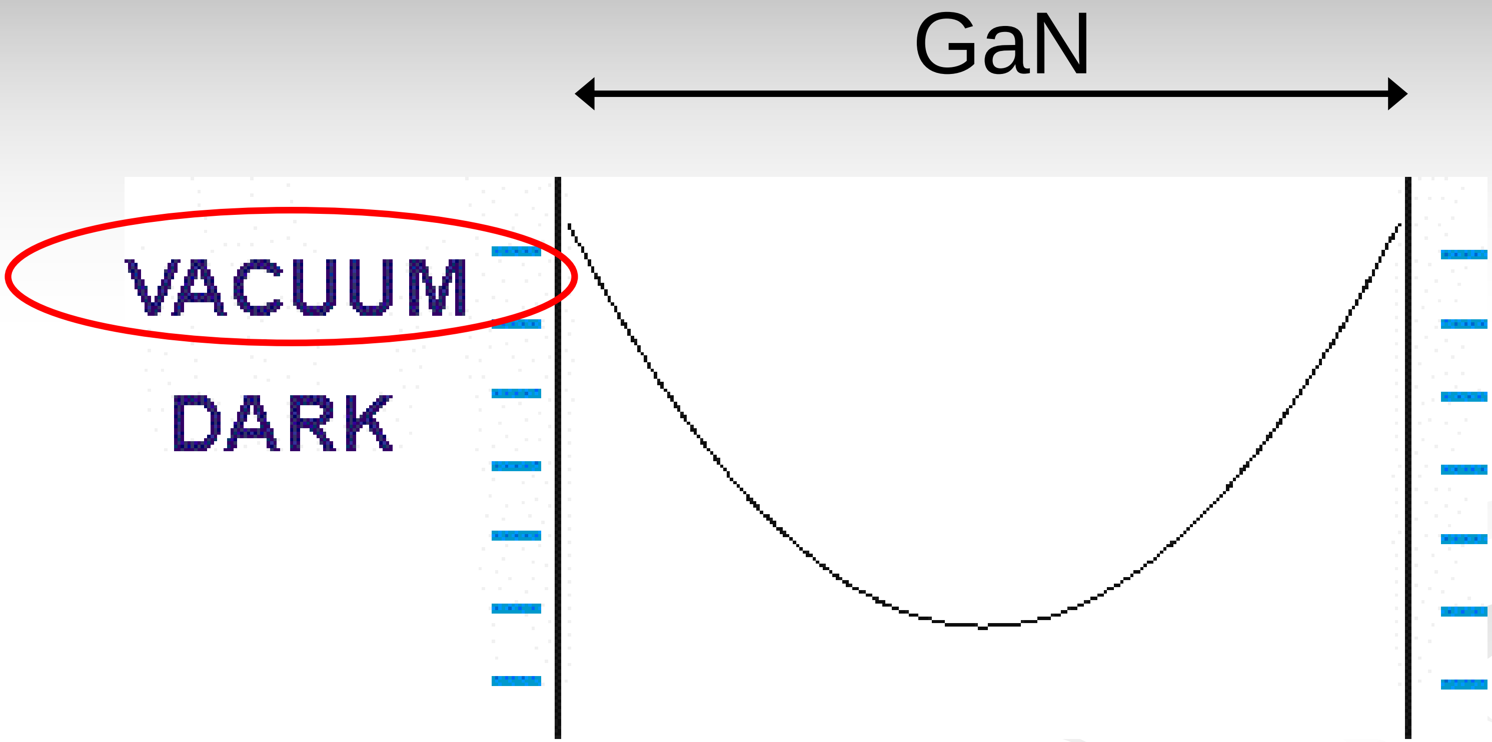
Surface Potential Barrier in Vacuum / Dark



Near-surface Band Bending ~1 eV

*R. Calarco et al. Nano Letters **5**, 981 (2005)*

*M. Foussekis et al., APL **94**, 162116 (2009)*

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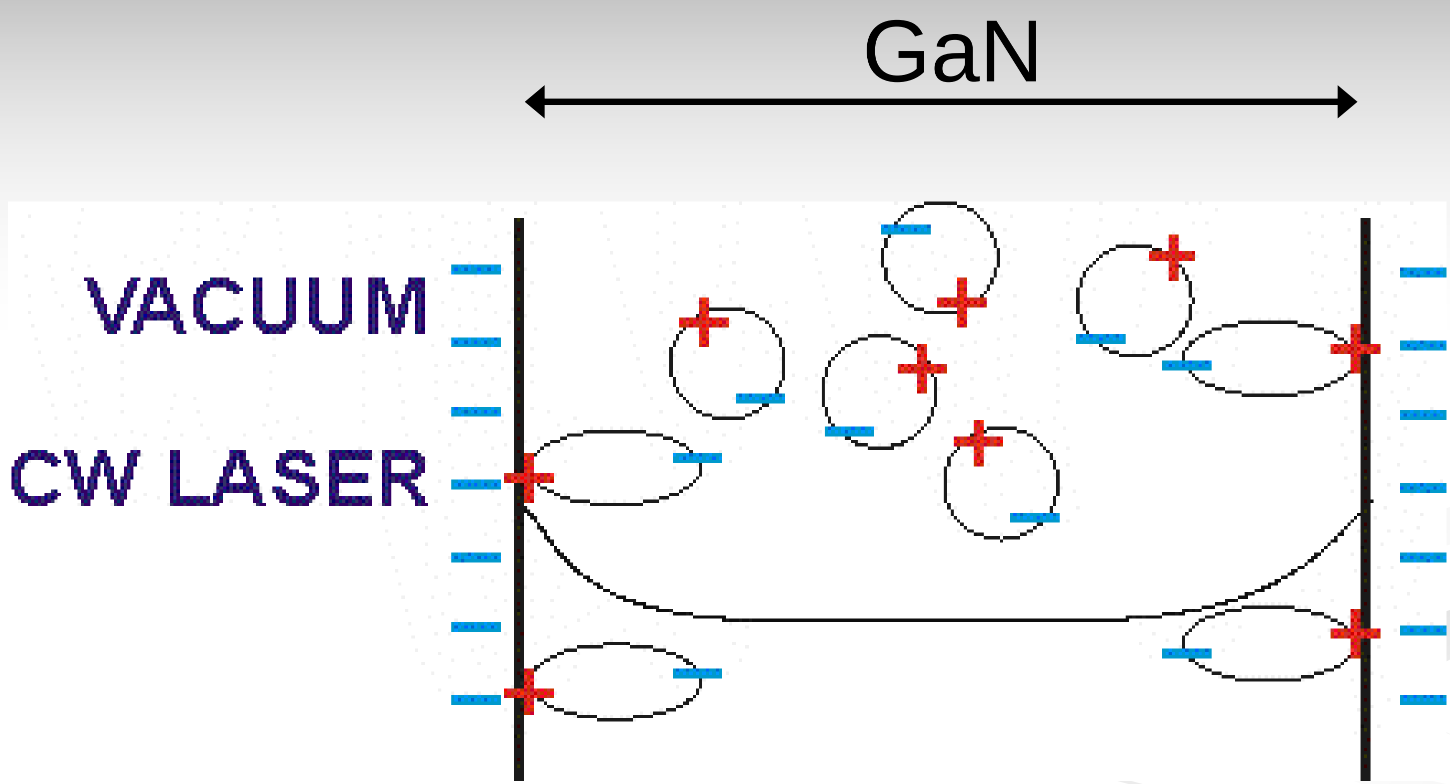
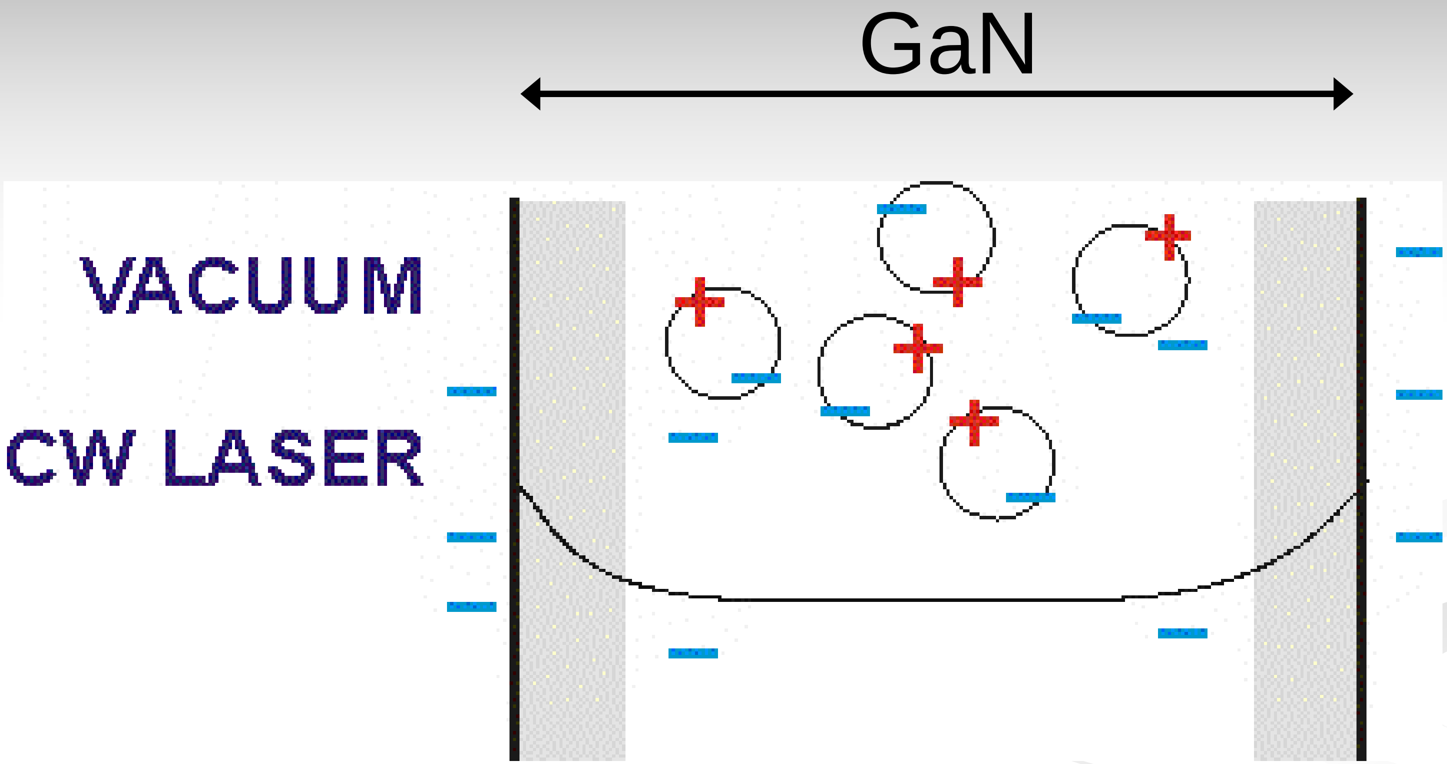
CW Creation / Recombination of Excitons



Partial neutralization of surface charge ⇒ narrow / shallow surface barrier where excitons cannot form

*Reshchikov et al., J. Vac. Sci. Technol. B **27**, 1688 (2009)*

CW Creation / Recombination of Excitons



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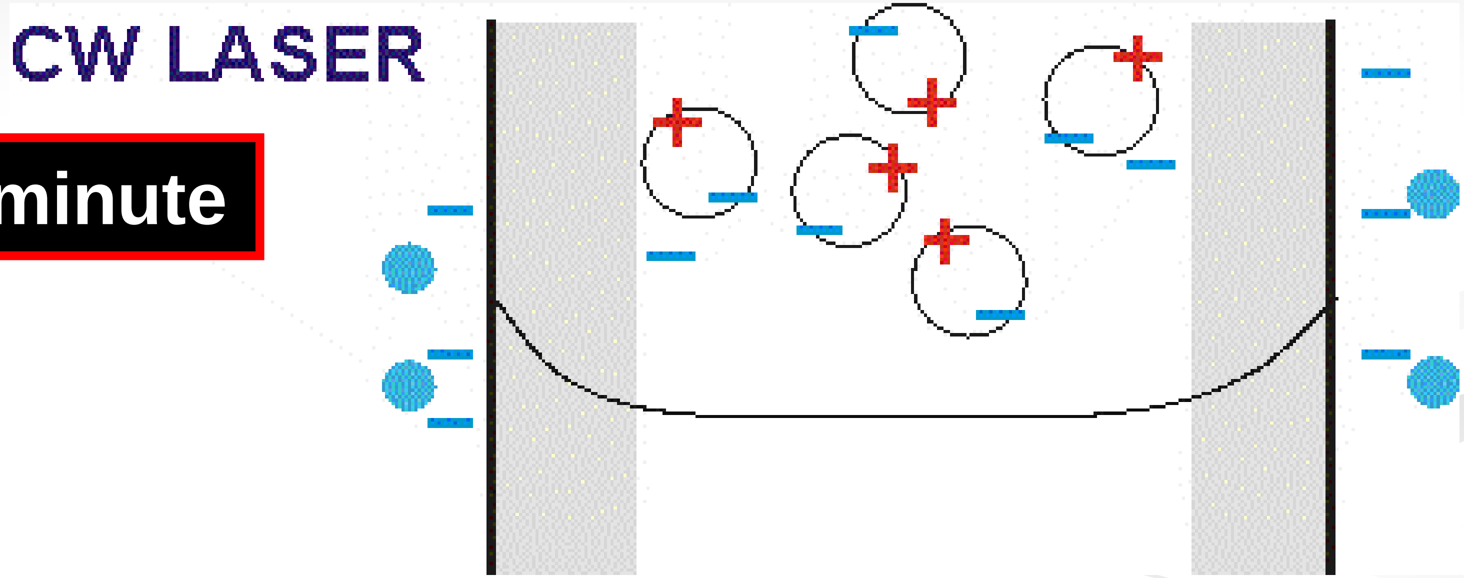
Electron tunneling and Oxygen Photoadsorption

GaN



Air 1 minute

Raising of a Higher / Wider Surface Barrier

*M.A. Reshchikov et al., J. Vac. Sci. Technol. B **27**, 1688 (2009)*

*M. Foussekis et al., APL **94**, 162116 (2009)*

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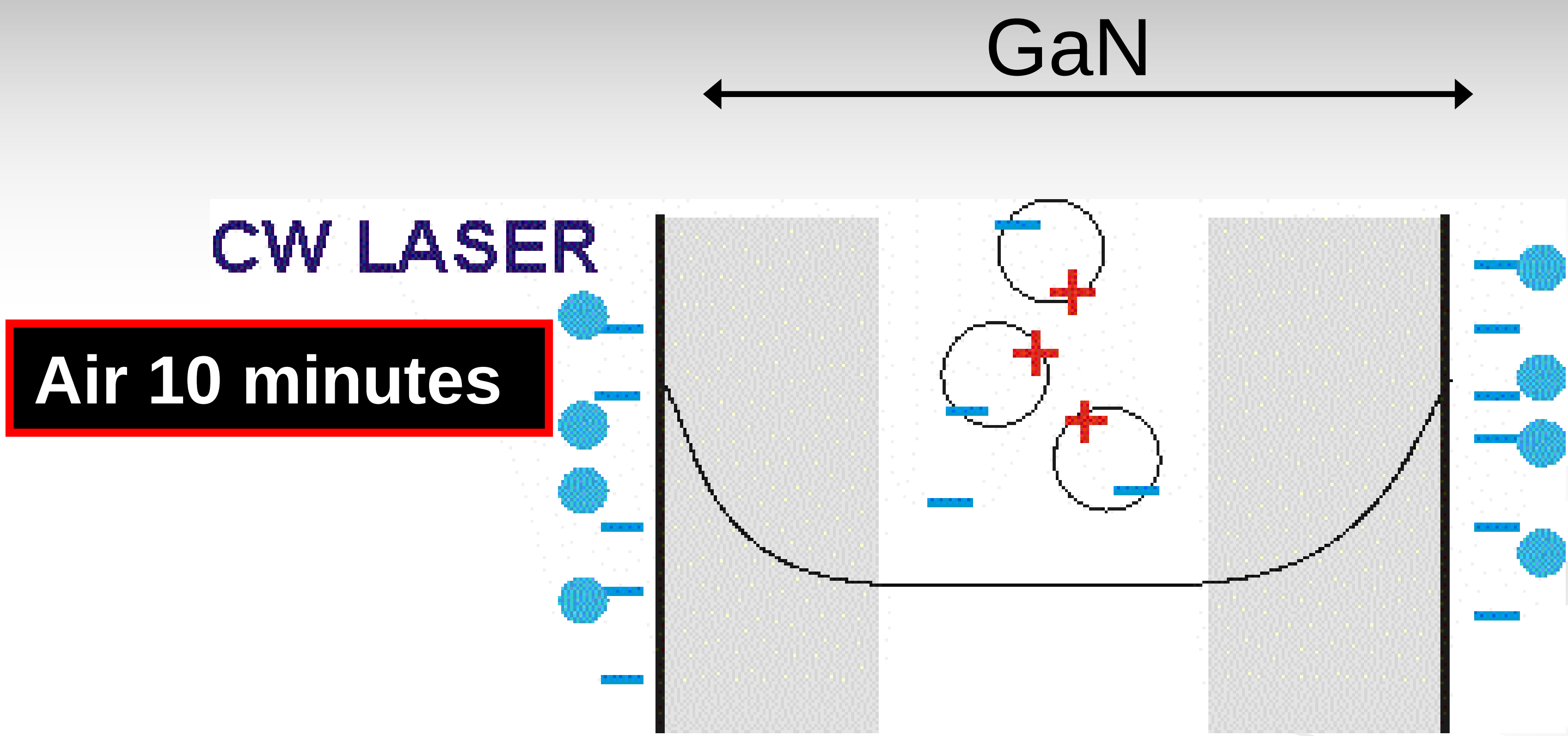
Self-Limited Photoadsorption

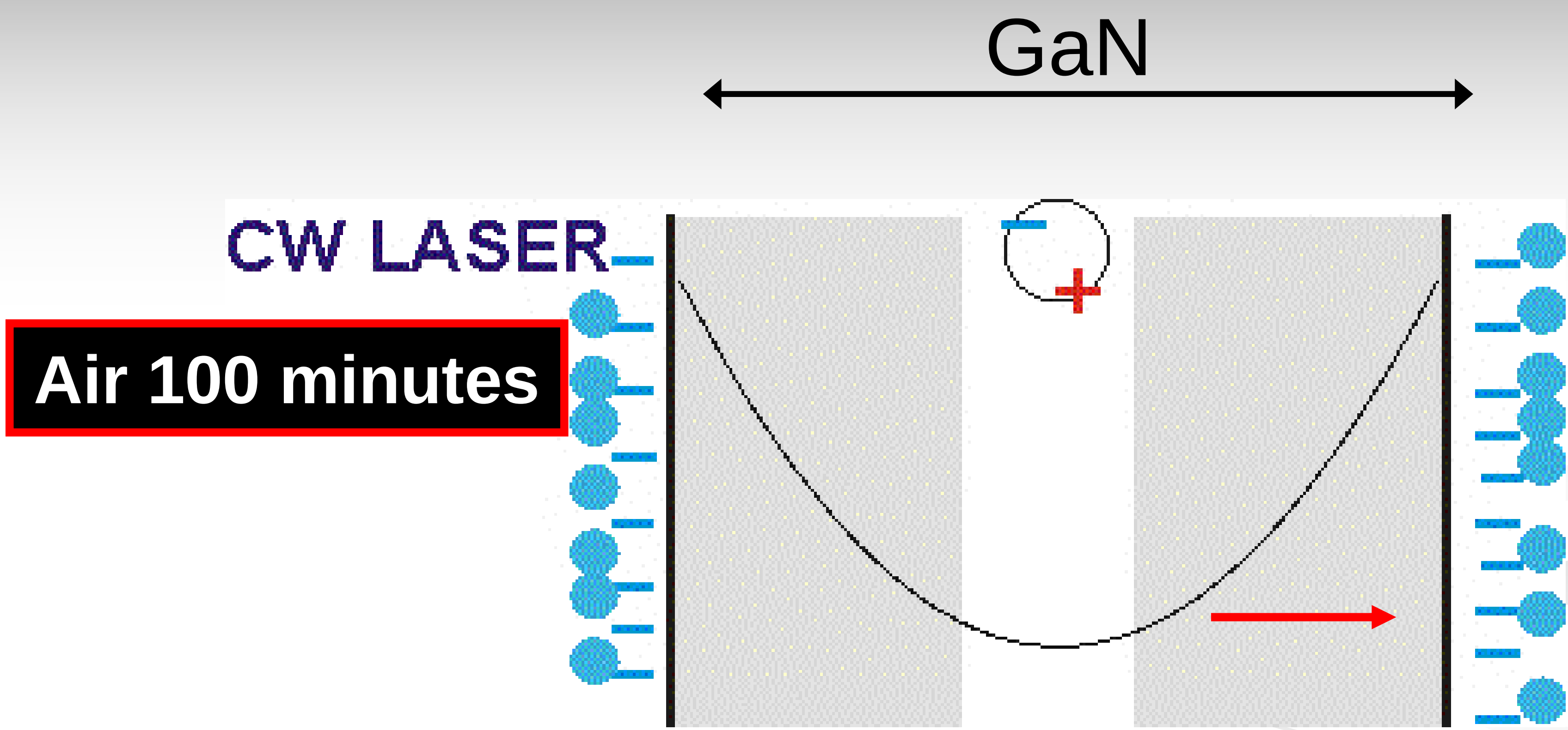


Wider barrier ⇒ Less charge tunneling ⇒ Less adsorption

*M.A. Reshchikov et al., J. Vac. Sci. Technol. B **27**, 1688 (2009)*

*M. Foussekis et al., APL **94**, 162116 (2009)*

Equilibrium: Maximized Surface Barrier

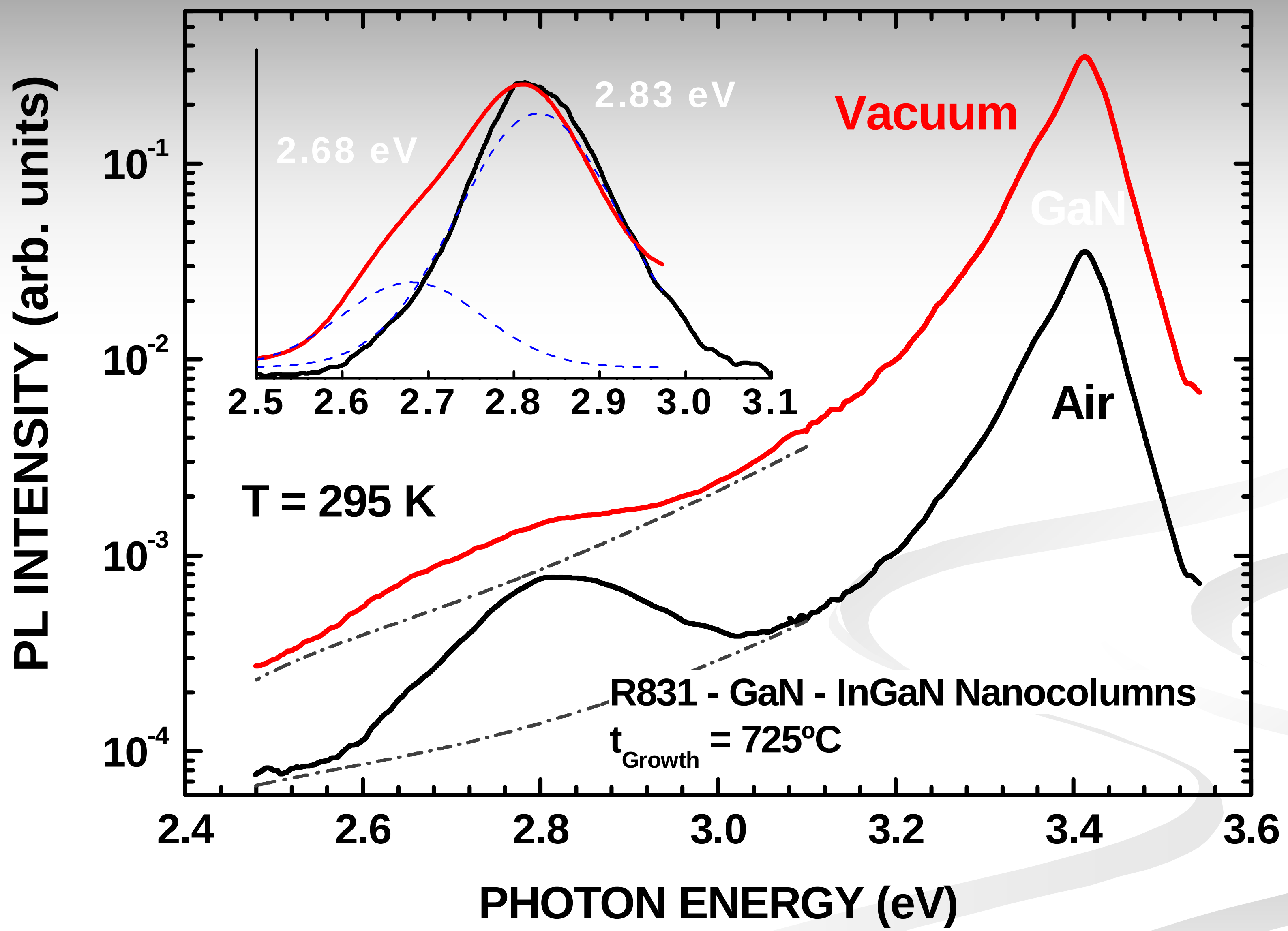


Minimum Volume for Exciton Recombination

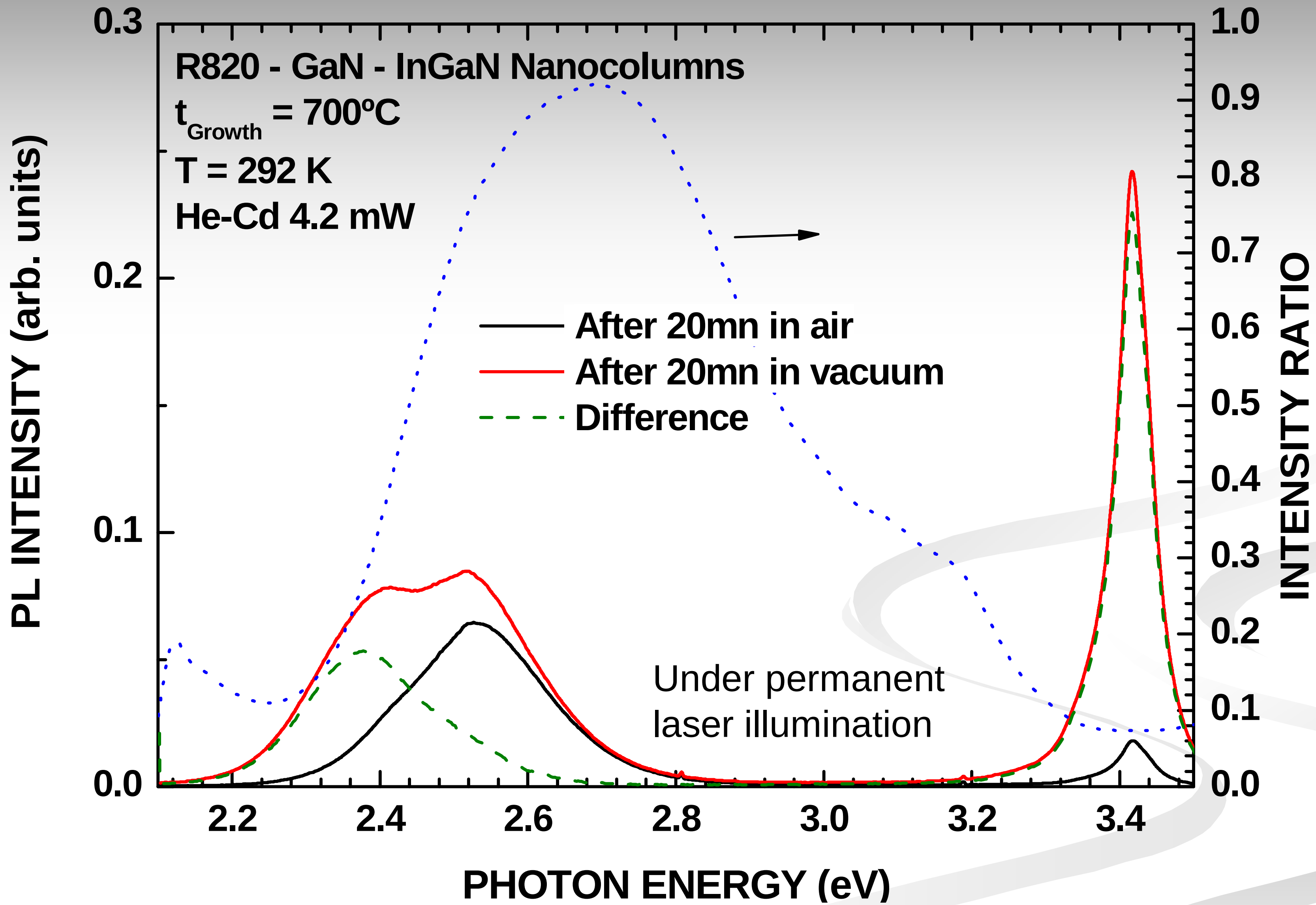
*M.A. Reshchikov et al., J. Vac. Sci. Technol. B **27**, 1688 (2009)*

*M. Foussekis et al., APL **94**, 162116 (2009)*

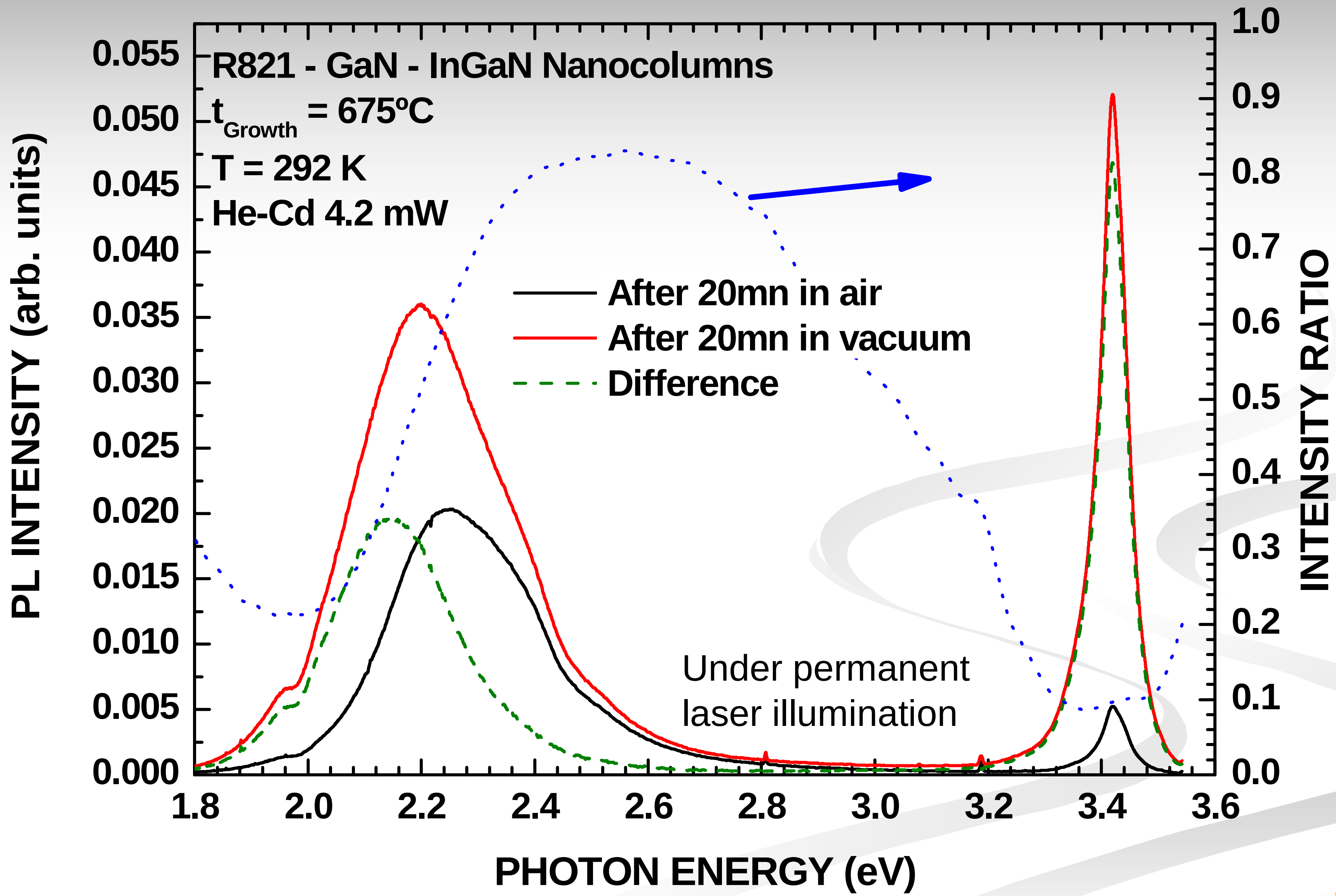
PL Quenching in Air: InGaN NCs. x = 0.10 (Violet)



PL Quenching in Air: InGaN NCs. x ~ 0.19 (Blue)



PL Quenching in Air: InGaN NCs. x = 0.28 (Green)



DISCUSSION

- **Much less quenching for InGaN NCs than for GaN NCs**

(1) *Effect of carrier localization ?* Needs more field to ionize localized excitons…

(2) Different Surface Behavior regarding Oxygen Adsorption

(3) Larger residual doping / Different Pinning of Fermi Level

- **NO quenching at higher energy / STRONG quenching at lower energy**

(1) Larger In content close to surface

(2) Radial Strain Gradient

SUMMARY

- Growth an PL characteristics of InGaN-on-GaN Nanocolumns
- Control of In content with preserved NC morphology
- Reversible PL quenching by 90% in GaN NCs when exposed to air (Photo-adsorption / desorption of oxygen)
- Almost *NO* PL quenching in InGaN NCs
- Existence of lower-energy PL from InGaN NCs *with* quenching

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